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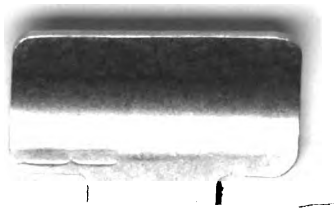
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Principles of thermodyna...

George Alfred Goodenough

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PRINCIPLES

OF

THERMODYNAMICS

BY

G. A. GOODENOUGH, M.E.

PROFESSOR OF THERMODYNAMICS IN THE UNIVERSITY OF ILLINOIS

THIRD EDITION, REVISED



NEW YORK

HENRY HOLT AND COMPANY

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1920

PREFACE

This edition includes the subject matter of the first edition, entirely rewritten and rearranged, and in addition a considerable part of the material that was originally intended for a second volume on heat engines. The result is practically a new book. A new title, "thermodynamics and heat engines," might describe more accurately the purpose and scope of the book; since, however, the stress has been laid on principles rather than facts, even in the applications, the earlier title has been retained as sufficiently indicative of the character of the work.

In the rewriting of the text the author has kept in view three principal objects. 1. To simplify and at the same time strengthen the presentation of the fundamental laws. In the earlier chapters the arrangement has been changed and more stress has been laid on important topics. The treatment of available energy and entropy, chapter V, has been worked out with special care. 2. To bring the book up to date. 3. To give an adequate presentation of the applications of thermodynamics to heat engines, air compression, and refrigeration. Considerable additions have been made to the subject matter, and a separate chapter has been devoted to each of the important applications. In the discussion of internal combustion engines the conventional "air standard" treatment has been replaced by a fairly accurate analysis.

As in the first edition, the text is copiously illustrated by problems, and in many cases the solutions are given in detail to show the student proper methods of computation. The number of exercises has been largely increased. The lists of references have been revised and brought up to date.

The author acknowledges his indebtedness to the standard books on thermodynamics and heat engines, in particular the works of Bryan, Preston, Griffiths, and Lorenz. He also acknowledges the generosity of manufacturers in supplying material for illustrations.

G. A. GOODENOUGH.

URBANA, ILL.,
June, 1920.

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SYMBOLS

NOTE. The following list gives the symbols used in this book. In case a magnitude is dependent upon the weight of the substance, the small letter denotes the magnitude referred to unit weight, the capital letter the same magnitude referred to M units of weight. Thus q denotes the heat absorbed by one pound of a substance, $Q = Mq$, the heat absorbed by M pounds.

J, Joule's equivalent.
A, reciprocal of Joule's equivalent.
M, weight of system under consideration.
t, temperature on the F. or the C. scale.
T, absolute temperature.
p, pressure.
v, V, volume.
γ, specific weight; also heat capacity.
u, U, intrinsic energy of a system.
i, I, heat content at constant pressure.
s, S, entropy.
W, external work.
q, Q, heat absorbed by a system from external sources.
h, H, heat generated within a system by irreversible transformation of work into heat.
c, specific heat.
c_v, specific heat at constant volume.
c_p, specific heat at constant pressure.
k, ratio c_p/c_v.
B, constant in the gas equation $pv = BT$.
R, universal gas constant.
n, exponent in equation for polytropic change, $pV^n = C$.
m, molecular weight.
$a_1, a_2 \ldots$, atomic weights.
H_m, heating value of a fuel mixture.
x, quality of a vapor mixture (p. 165).
q', heat of the liquid.
q'', total heat of saturated vapor.
r, latent heat of vaporization.
ρ, internal latent heat.
ψ, external latent heat.

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v', v'', specific volume of liquid and of vapor, respectively.
u', u'', internal energy of liquid and of vapor, respectively.
s', s'', entropy of liquid and of vapor, respectively.
i', i'', heat content of liquid and of vapor, respectively.
c', c'', specific heat of liquid and of vapor, respectively.
ϕ, humidity.
w, velocity of flow.
w_a, acoustic velocity.
F, area of cross-section of channel.
z, work of overcoming friction in the flow of fluids.
p_m, critical pressure (flow of fluids).
μ, Joule-Thomson coefficient.
η, efficiency of a heat engine.
N, steam consumption per h.p.-hour.

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PRINCIPLES OF THERMODYNAMICS

CHAPTER I

ENERGY TRANSFORMATIONS

1. Scope of Thermodynamics.—In the most general sense, thermodynamics is the science that deals with energy. Since all natural phenomena, all physical processes, involve manifestations of energy, it follows that thermodynamics is one of the most fundamental and far-reaching of the physical sciences. Thermodynamics lies at the foundation of a large region of physics and also of a large region of chemistry; and it stands in a more or less intimate relation with other sciences.

In a more restricted sense, thermodynamics is that branch of physics which deals specially with heat energy and its transformations into other forms of energy. It develops the laws that govern such transformations, and investigates the properties of the media by which the transformations are effected. In technical thermodynamics the general principles thus developed are applied to the problems presented by the various heat motors.

2. Energy.—A body or system of bodies is said to possess **energy** when by virtue of its condition the body or system is capable of doing mechanical work while undergoing a change of state. Many illustrations of this statement will occur to the reader. A moving body is capable of doing work in coming to rest, that is, in changing its state as regards velocity; a body in an elevated position can do work in changing its position; a heated metal rod is capable of doing mechanical work when it contracts in cooling. In each case some change in the state of the body results in the doing of work; hence, in each case the body in question possesses energy.

Energy, like motion, is purely relative. It is impossible to give a numerical value to the energy of a system without referring it to some standard system, whose energy we may arbitrarily assume to be zero. For example, the energy of the water

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in an elevated reservoir is considered with reference to the energy of an equal quantity at some chosen lower level. The kinetic energy of a body moving with a definite velocity is compared with that of a body at rest on the earth's surface, and having, therefore, zero velocity relative to the earth. The energy of a pound of steam is referred to that of a pound of water at the temperature of melting ice.

3. Mechanical Energy is that possessed by a body or system due to the motion or position of the body or system relative to some standard of reference. Mechanical **kinetic** energy is that due to the motion of a body and is measured by the product $\frac{1}{2}mw^2$, where m denotes the mass of the body and w its velocity relative to the reference system. It should be observed that $\frac{1}{2}mw^2$ is a scalar, not a vector quantity, and it must be considered positive in sign. Hence, if a system consists of a number of masses $m_1, m_2, \ldots, m_n$ moving with velocities $w_1, w_2, \ldots, w_n$, respectively, the total kinetic energy of the system is the sum

$$\tfrac{1}{2}(m_1w_1^2 + m_2w_2^2 + \ldots + m_nw_n^2) = \tfrac{1}{2}\Sigma mw^2,$$

independently of the directions of the several velocities.

The mechanical **potential** energy of a system is that due to position or configuration, and may be defined as the work the system can do in passing from its given position or configuration to a standard reference position or configuration. Examples of systems having mechanical potential energy are seen in elevated reservoirs of water, stretched or compressed springs, etc.

4. Intrinsic Energy of a System.—In the study of the dynamics of a material system the conceptions of mechanical kinetic and potential energy are sufficient, provided frictional effects are excluded. To explain *all* the changes that take place when a system does work or has work done on it, it is necessary, however, to take into consideration another kind of energy, the internal energy of the system due to its molecular state.

According to the molecular theory all bodies consist of very small parts called molecules, and these are assumed to be in a state of incessant motion. Depending on the character of this molecular motion, a body has one of three states of aggregation,

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namely; solid, liquid, and gaseous. In the solid state each molecule is confined to a small region which it never leaves but it is supposed to oscillate around a mean position. If for some reason the molecular agitation is increased beyond a certain limit the molecules break loose from their constraint, and while a molecule is still under the influence of neighboring molecules it may have a motion of translation as well as vibration and wander in a haphazard way through the aggregate of molecules. The body is now in the liquid state. While the molecules have more freedom in the liquid than in the solid state, they are still relatively close together as in the solid. The passage from the solid to the liquid state involves no marked change in the total volume of the body.

If now the molecular velocities in the liquid are increased a point is reached such that a molecule at the surface of the liquid may project itself into the space above the liquid thus overcoming the attraction of the neighboring molecules in surface layer. As the process continues the space above the liquid is filled with molecules each of which has a free path and is outside the influence of other molecules. When all of the molecules of the liquid have thus passed from the surface, the substance has been changed from the liquid to the gaseous state. The passage from the liquid to the gaseous state usually involves a large increase of volume.

The changes of state outlined in the preceding paragraphs evidently involve changes of energy. Each molecule being in motion possesses kinetic energy. If the velocity of the molecule is denoted by w and the mass of the molecule by m, the kinetic energy is $\frac{1}{2}mw^2$. In the given system the multitude of molecules have different velocities and are moving in different directions. Nevertheless, the summation $\Sigma\frac{1}{2}mw^2$ extended to all the molecules of the system gives a definite amount of kinetic energy. In the case of a gaseous system the molecule, in addition to the translation with velocity w, may have a vibratory motion and also a motion of rotation. It will therefore possess additional kinetic energy due to these motions.

When the molecular velocities are increased the molecular kinetic energy is likewise increased; therefore energy must have been brought into the system from outside. Also when the body changes its state of aggregation, as from solid to liquid or

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from liquid to gas, energy must be supplied to effect the change. Thus work must be done to overcome the forces that hold the molecules confined in the solid state and break up the molecular structure; likewise work must be done in separating the molecules of a liquid against their mutual attraction in the change to the gaseous state. The work thus performed is stored in the system as molecular potential energy.

Even without a change of aggregation potential energy may be stored in a body. Consider the case of a gas having initially a volume V_1, and suppose that the volume is increased to V_2. The molecules, on the whole, are farther apart in the second state and have therefore been separated. Though the molecules are relatively far apart there are still attractive forces between them, and work must be done in separating them in opposition to these forces. This work is stored as potential energy.

The energy of a system due to its molecular motion or configuration is called the **intrinsic energy** and is denoted by the symbol U. The increase of intrinsic energy ΔU may be divided into two parts: ΔK, the increase of kinetic energy when the molecular velocity is increased, and ΔP, the increase of potential energy due to a change in the state of aggregation (melting or vaporization) or to an increase in the volume of the system.

5. Temperature.—The word temperature is used to indicate the hotness of a body. A hot body is said to have a high temperature, a cold body a low temperature. A scale of temperature may be established by making use of the fact that certain bodies expand as they become hotter. For ordinary purposes the substance chosen for this purpose is mercury enclosed in glass; and the change in temperature is indicated by the expansion (or contraction) of the mercury.

The molecular kinetic theory of gases furnishes a useful conception of temperature. According to this theory, the temperature of a gas is associated with the mean molecular kinetic energy. Increase of molecular speed, that is, increase of kinetic energy, is accompanied by rise in temperature, and vice versa. The same conclusion may be extended to liquid and solid bodies.

6. Heat.—It is observed that when two bodies having different temperatures are placed in contact the temperature of the

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warmer falls, that of the colder rises, and the change continues until the two bodies attain the same temperature. To account for this phenomenon we say that **heat** flows from the hotter to the colder body. The fall of temperature of one body is due to the loss of heat, while the rise in temperature of the other is due to the heat received by it. It is to be noted that the change of temperature is the thing observed and that the idea of heat is introduced to account for the change, just as in dynamics the idea of force is introduced to account for the observed motion of bodies. Whatever may be the nature of heat, it is evidently something measurable, something possessing the characteristics of quantity.

In the old caloric theory, heat was assumed to be an imponderable, all-pervading fluid which could pass from one body to another and thus cause changes of temperature. The experiments of Rumford (1798), Davy (1812), and Joule (1840) showed the falsity of the caloric theory and established the identity of heat with molecular energy.

Let us consider what happens when body A with a higher temperature is placed in contact with body B at lower temperature. The higher temperature of body A indicates that the mean speed of the molecules of body A is greater than that mean speed of the molecules of body B. When the two bodies are placed in contact the molecules of A impart motion to the molecules of B. The mean molecular speed in A decreases, that in B increases until equilibrium is established. What has flowed from A to B is molecular energy; the body A has lost intrinsic energy ΔU which has passed into body B. All of the energy ΔU entering body B may be expended in raising the temperature of B, that is, in increasing the molecular kinetic energy; on the other hand, if body B experiences a change of state of aggregation, as melting or vaporization, part or all of the energy received may be expended in doing the work required in the change of molecular structure. This energy is stored in body B as potential energy. The term *latent heat* is frequently applied to the energy thus used to change the molecular structure and stored as potential energy, while the term *sensible heat* is applied to the energy that goes to increase the molecular kinetic energy of the system. The sensible heat manifests itself by a rise in temperature of the

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system receiving it; the latent heat does not involve a change of temperature.

7. Units of Heat.—Heat may be measured by the effects produced by it upon substances. Two of the most marked effects are: rise of temperature; change of state of aggregation, as in the melting of ice or vaporization of water. Hence, there are two possible means of establishing a unit of heat:

1. The heat required to raise a given mass of a selected substance, as water, through a chosen range of temperature may be taken as the unit.

2. The quantity of heat required to change the state of aggregation of some substance, as, for example, to melt a given weight of ice, may be taken as the unit.

According to Griffiths, *the standard thermal unit is the heat required to raise* 1 *gram of water from* 17° *to* 18° *C. on the Paris hydrogen scale, or one fifth of the amount to raise it from* 15° *to* 20° *C. on the same scale.* This thermal unit is called the gram-calorie, or the small calorie. If the weight of water is taken as 1 kilogram, the resulting unit is the kilogram-calorie or large calorie. This is the unit employed by engineers.

The **British thermal** (B. t. u.) is defined as *the heat required to raise the temperature of* 1 *pound of water from* 63° *to* 64° *F.*

The unit thus defined is practically identical with the **mean B. t. u.** which is defined as the $\frac{1}{180}$ part of the heat required to raise the temperature of one pound of water from 32° F. to 212° F.

8. Relation between Heat and Work.—It is a matter of common experience that heat may be produced by mechanical work. Work is expended in overcoming the friction between the contact surfaces of the moving parts of machines and the journals and bearings show a rise of temperature. The metal chips from a lathe or planer are hot, showing that the work of driving the machine has been transformed into the heat required to produce the rise in temperature. The temperature of air is raised by compression.

Conversely, work may be obtained by the expenditure of heat, as is exemplified in the steam engine and other heat engines. Thus in the steam engine the steam in expanding partly condenses and at the same time has its temperature decreased. According

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to the molecular theory, therefore, the steam gives up some of its molecular kinetic energy and also some of its molecular potential energy (latent heat) due to condensation. The heat energy thus given up is transformed into the work that is obtained from the engine.

According to the law of conservation of energy the heat that is produced is the equivalent of the work that is expended; or in the case of the heat engine, the work obtained is the equivalent of the heat that disappears. The heat is measured by one unit, the B. t. u., the work by another unit, the foot pound; hence, if the dynamical theory is valid, there should be a fixed invariable relation between these two units. That such a relation exists was first conclusively shown by the experiments of Dr. Joule of Manchester, which were begun in 1840 and were prosecuted through several years.

In Joule's[1] experiments work was expended in stirring water by means of a revolving paddle. From the rise of temperature of the known weight of water, the heat energy developed could be expressed in thermal units; and a comparison of this quantity with the measured quantity of work supplied gave immediately the desired value of the ratio between the two units.

Professor Rowland (1878–1879) used the same method, but by driving the paddle wheel with a petroleum engine he was enabled to supply a much larger quantity of mechanical energy to the water, and the influence of various corrections was correspondingly decreased. Rowland's results are justly given great weight in deducing the finally accepted value of the equivalent.

Another result of the highest value is that found by Reynolds and Moorby (1897). The work of a 100 horsepower engine was absorbed by a hydraulic brake. Water entered the brake at or near 0° C. and was run through it at a rate that caused it to emerge at a temperature of about 100° C. In this way the mechanical equivalent of the heat required to raise the temperature of one pound of water from 0° to 100° C. was determined.

Of the experiments by the indirect method those of Griffiths

[1] For a very full description of the experiments made to determine the mechanical equivalent and a searching discussion of the results, the reader is referred to Griffiths' book, *The Thermal Measurement of Energy*.

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(1893), Schuster and Gannon (1894), and Callendar and Barnes (1899) deserve mention. In each set of experiments the heat developed by an electric current was measured and compared with the electrical energy expended.

From a careful comparison of the results of the most trustworthy experiments, Griffiths has decided that the most probable value of the ratio between the two units is:

1 B. t. u. = 777.64 foot-pounds.

The number 777.64 is called the mechanical equivalent of heat and it is denoted by the symbol J. The reciprocal of J, is usually denoted by A. Evidently A is the heat equivalent of a unit of work, that is

$$1 \text{ ft. lb.} = A \text{ B. t. u.}$$

9. Other Forms of Energy.—In addition to heat and mechanical energy, there are other forms of energy that require consideration. The energy stored in fuel or in explosives may be considered potential **chemical** energy. **Electrical** energy is exemplified in the electric current and in the electrostatic charge in a condenser. Other forms of energy are associated with wave motions either in ordinary fluid media or in the ether. Sound, for example, is a wave motion usually in air. Light and radiant heat are wave motions in the ether.

10. Transformations of Energy.—Attention has been called to the generation of heat energy by the expenditure of mechanical work. This is only one of a great number of energy changes that are continually occurring. We see everywhere in everyday life one kind of energy disappearing and another form simultaneously appearing. In a power station, for example, the potential energy stored in the coal is liberated and is used up in adding heat energy to the water in the boiler. Part of this heat energy disappears in the engine and its equivalent appears as mechanical work; finally, this work is expended in driving a generator, and in place of it appears electric energy in the form of the current in the circuit. We say in such cases that one form of energy is transformed into another. The following are a few familiar examples of energy transformations; many others will occur to the reader.

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Mechanical to heat: Compression of gases; friction; impact.
Heat to mechanical: Steam engine; expansion and contraction of bodies.
Mechanical to electrical: Dynamo; electric machine.
Electrical to mechanical: Electric motor.
Heat to electrical: Thermopile.
Electrical to heat: Heating of conductors by current.
Chemical to electrical: Primary or secondary battery.
Electrical to chemical: Electrolysis.
Chemical to thermal: Combustion of fuel.

11. Conservation of Energy.—Experience points to a general principle underlying all transformations of energy.

The total energy of an isolated system remains constant and cannot be increased or diminished by any physical processes whatever.

In other words, energy, like matter, can be neither created nor destroyed; whenever it apparently disappears it has been transformed into energy of another kind.

This principle of the conservation of energy was first definitely stated by Dr. J. R. Meyer in 1842, and it soon received confirmation from the experiments of Joule on the mechanical equivalent of heat. The conservation law cannot be proved by mathematical methods. Like other general principles in physics, it is founded upon experience and experiment. So far, it has never been contradicted by experiment, and it may be regarded as established as an exact law of nature.

A perpetual motion *of the first class* is one that would supposedly give out energy continually without any corresponding expenditure of energy. That is, it would create energy from nothing. A perpetual-motion engine would, therefore, give out an unlimited amount of work without fuel or other external supply of energy. Evidently such a machine would violate the conservation law; and the statement that perpetual motion of the first class is impossible is equivalent to the statement of the conservation principle.

12. Degradation of Energy.—While one form of energy can be transformed into any other form, all transformations are not effected with equal ease. It is only too easy to transform mechanical work into heat; in fact, it is one duty of the engineer

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to prevent this transformation as far as possible. Furthermore, of a given amount of work *all* of it can be transformed into heat. The reverse transformation, on the other hand, is not easy of accomplishment. Heat is not transformed into work without effort, and of a given quantity of heat only a part can be thus transformed, the remainder being inevitably thrown away. All other forms of energy can, like mechanical energy, be completely converted into heat. Electrical energy, for example, in the form of a current, can be thus completely transformed. Comparing mechanical and electrical energy, we see that they stand on the same footing as regards transformation. In a perfect apparatus mechanical work can be completely converted into electrical energy, and, conversely, electric energy can be completely converted into mechanical work.

We are thus led to a classification of energy on the basis of the possibility of complete conversion. Energy that is capable of complete conversion, like mechanical and electrical energy, we may call **high-grade** energy; while heat, which is not capable of complete conversion, we may call **low-grade** energy.

There seems to be in nature a universal tendency for energy to degenerate into a form less available for transformation. Heat will flow from a body of higher temperature to one of lower temperature with the result that a smaller fraction of it is available for transformation into work. High-grade energy tends to degenerate into low-grade heat energy. Thus work is degraded into heat through friction, and electrical energy is rendered unavailable when transformed into heat in the conducting system. Even when one form of high-grade energy is transformed into another, there is an inevitable transformation of some part of the high-grade energy into heat. Thus in the electric motor a small percentage of the electric energy supplied is wasted in friction; in the case of chemical reactions the chemical energy of the products is less than that of the original substances, the difference being due to the heat developed during the reaction. As Griffiths aptly says: "Each time we alter our investment in energy, we have thus to pay a commission, and the tribute thus exacted can never be wholly recovered by us and must be regarded, *not* as destroyed, but as thrown on the waste-heap of the Universe."

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The terms **degradation of energy, dissipation of energy,** and **thermodynamic degeneration** are applied by different writers to this phenomenon that we have just described. The principle of degradation of energy may be stated as follows:

Every natural process is accompanied by a certain degradation of energy or thermodynamic degeneration.

The principle of the degradation of energy denies the possibility of perpetual motion *of the second class,* which may be described as follows: A mechanism with friction is inclosed in a case through which no energy passes. Let the mechanism be started in motion. Because of friction, work is converted into heat, which remains in the system, since no energy passes through the case. Suppose now that the heat thus produced can be transformed completely into work; then the work may be used again to overcome friction and the heat thus produced can be again transformed into work. We then have a perpetual motion in a mechanism with friction without the addition of energy from an external source. Such a mechanism does not violate the conservation law, since no energy is created. It, however, is just as much an absurdity as the perpetual motion of the first-class because it violates the principle of degradation.

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CHAPTER II

THE ENERGY EQUATION. THERMAL CAPACITIES

13. Thermodynamic Systems.—A thermodynamic system may be defined as a body or system of bodies capable of receiving and giving out heat or other forms of energy. As examples of thermodynamic systems, we may mention the media used in heat motors: water vapor, air, ammonia, etc.

We are frequently concerned with changes of state of systems, for it is by such changes that a system can receive or give out energy. We assume ordinarily that the system is a homogeneous substance of uniform density and temperature throughout; also that it is subjected to a uniform pressure. Such being the case, the state of the substance is determined by the mass, temperature, density, and external pressure. If we direct attention to some fixed quantity of the substance, say a unit mass, we may substitute for the density its reciprocal, the volume of the unit mass; then the three determining quantities are the temperature, volume, and pressure. These physical magnitudes which serve to describe the state of a substance are called the **coördinates** of the substance.

In all cases, it is assumed that the pressure is uniform over the surface of the substance in question and is normal to the surface at every point; in other words, hydrostatic pressure. We may consider this pressure in either of two aspects: it may be viewed as the pressure *on* the substance exerted by some external agent, or as the pressure exerted *by* the substance on whatever bounds it. For the purpose of the engineer, the latter view is the most convenient, and we shall always consider the pressure exerted *by* instead of *on* the substance. The pressure is always stated as a *specific* pressure, that is, pressure per unit of area, and is denoted by p. The unit ordinarily used is the pound per square foot.

The volume of a unit weight of the substance is the *specific volume*. If volumes are expressed in cubic feet then the specific

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volume is the number of cubic feet occupied by a pound. As it is frequently necessary to distinguish between the specific volume and the volume of any given weight of the substance, we shall use v to denote the former and V the latter. Thus, in general, v will denote the volume of one pound of the substance, V the volume of M pounds; hence

$$V = Mv.$$

The convention of small letters for symbols denoting quantities per unit weight and capitals for quantities associated with any other weight M will be followed throughout the book. Thus q will denote the heat applied to one pound of gas and Q the heat applied to M pounds, u the energy of a unit weight of substance, U the energy of M units, etc.

As regards the third coördinate, temperature, we shall accept for the present the scale of the air thermometer. Later the absolute or thermodynamic scale will be introduced.

14. Characteristic Equation.—In general, we may assume the values of any two of the three coördinates p, v, T, and then the value of the third will depend upon values of these two. For example, let the system be one pound of air inclosed in a cylinder with a movable piston. By loading the piston we may keep the pressure at any desired value; then by the addition of heat we may raise the temperature to any predetermined value. Thus we may fix p and T independently. We cannot, however, at the same time give the volume v any value we please; the volume will be uniquely determined by the assumed values of p and T, or in other words, v is a function of the independent variables p and T. In a similar manner we may take p and v as independent variables, in which case T will be the function, or we take v and T as independent and p as the function depending on them.

For any substance, therefore, the coördinates p, v, and T are connected by some functional relation, as

$$p = f(v,T).$$

The equation giving this relation is called the **characteristic equation** of the substance. The form of the equation must be determined by experiment.

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For some substances more than one equation is required; thus for a mixture of saturated vapor and the liquid from which it is formed, the pressure is a function of the temperature alone, while the volume depends upon the temperature and a fourth variable expressing the relative proportions of vapor and liquid.

15. The First Law of Thermodynamics.—The principle of conservation of energy applied to the conversion of heat into work is the first law of thermo-dynamics. The law may be stated in the following words: *When work is expended in producing heat, the quantity of heat generated is proportional to the work done, and conversely, when heat is employed to do work, a quantity of heat precisely equivalent to the work done disappears.*

If we denote by Q the heat converted into work and by W the work thus obtained, we have as symbolic statements of the first law,

$$W = JQ, \text{ or } Q = AW,$$

in which J denotes Joule's equivalent, and $A = \frac{1}{J}$. If Q is expressed in B. t. u. and W in foot pounds, $J = 777.64$ (Art. 8).

16. Various Equivalents.—While the foot-pound is the conventional unit of work in the English system of units, other units may be employed. The *erg*, the absolute unit of the C. G. S. system is too small for practical use, but the *joule*, which is 10^7 ergs, is a convenient unit, though it is restricted chiefly to the measurement of electrical energy. In the metric system the *kilogram-meter* is the unit of work. For expressing large quantities of work the *horsepower-minute*, the *horsepower-hour*, and the *kilowatt-hour* are frequently used. As units of heat we have, in addition to the B. t. u., the *gram-calorie* and the *kilogram-calorie*.

Having the one equivalent 777.64, the standard value of g, 32.174 ft./sec.^{2} (by international agreement), and the various conversion factors for the metric and English systems of units, the relations between the various energy units may be found. The following are important and should be memorized.

1 kilogram-calorie = 426.64 kilogram-meters

1 gram-calorie = 4.184 joules

1 horsepower-minute = 42.44 B. t. u.

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1 horsepower-hour = 2546.2 B. t. u.
1 kilowatt-hour = 3414.5 B. t. u.

17. The Energy Equation.—A thermodynamic system, as a given mass of gas or a mixture of vapor and liquid, absorbs heat from some external source. We consider the effects produced and the ways in which the energy thus absorbed may be expended.

A portion of the heat may be used in raising the temperature of the system. According to the dynamical theory, this portion is expended in increasing the kinetic energy of the system; it is stored in the system as so-called sensible heat. With the rise in temperature the volume of the system is, in general, increased, and as a consequence work must be done. If the system is subjected to an external pressure, work is done in opposition to the pressure when the volume is increased. This work is stored not in the system but in the surroundings; it is called the *external work*. In addition when the volume increases *internal work* is done against internal forces such as molecular attractions. If during the heating process there is a change of state of aggregation, as the vaporization of liquid, the internal work may be a large part of the energy received; otherwise it is small. The internal work is stored in the system as molecular potential energy.

Let dK denote the increase of thermal kinetic energy, dP the internal work or increase of thermal potential energy, and dW the external work. Then if dQ is the heat absorbed, we have

$$JdQ = dK + dP + dW. \tag{1}$$

The sum of the terms dK and dP is dU, the increase of the intrinsic energy of the system: hence

$$JdQ = dU + dW. \tag{2}$$

It is important to observe that of the energy JdQ received, the energy dU is stored in the system while the energy dW has passed out of the system and is stored in external systems.

The sign of dQ is considered as positive when heat is absorbed by the system, hence negative dQ indicates heat taken from the system. The work dW is regarded as positive when done *by* the system in expanding, therefore it is to be considered negative when done *on* the system, as in compression.

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18. External Work. Indicator Diagrams.—In general, the external work dW is the work done by the system in expanding against a uniform normal pressure. We assume that the pressure is the same at all parts of the system and equal to the external pressure. To arrive at a general expression for the work suppose the system (as air, or steam) to be confined in a cylinder with a movable piston, the area of which is A square units, and let the piston move a distance dx. If the pressure is p pounds per unit area, the force against which the piston moves is the product pA, and the work done is evidently

$$dW = pAdx.$$

But Adx is the increment of volume dV, hence

$$dW = pdV. \qquad (1)$$

Introducing this expression for dW in equation (2) preceding, we have

$$JdQ = dU + pdV. \qquad (2)$$

For a unit weight of the substance, we may write

$$Jdq = du + pdv. \qquad (3)$$

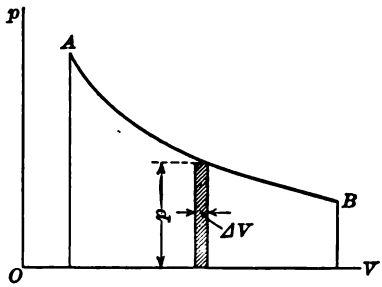


FIG. 1.

As thus written, the three terms of the equation are expressed in mechanical units, *i.e.*, foot pounds. If the energy u is expressed in thermal units (as B. t. u.) the equation takes the form

$$dq = du + Apdv. \qquad (4)$$

Let the pressure p (per unit area) and the volume V of the system be chosen as the independent coordinates, or variables. If a pair of axes be drawn and labeled p and V, Fig. 1, then the state of the system may be represented graphically by a point, as A, and a continuous change of state by a curve, as AB, described by the state-point. Diagrams thus drawn on the pV-plane are called *indicator diagrams.*

The area A_1ABB_1 included between the curve AB and the V-axis is obtained by the summation of elementary areas $p\Delta V$ and is therefore expressed by the definite integral $\int_{V_1}^{V_2} pdV$. From

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equation (1) this integral gives the external work done by the system during the change of state; hence the external work is represented graphically by the area between the path on the pV-plane and the V-axis.

19. Cyclic Transformation.—If the system, starting from a given state, is made to pass through a series of changes but ultimately returns to the initial state, it is said to perform a *cycle*. The indicator diagram for the cycle is a closed curve on the pV-plane. We denote by (W) the external work done in traversing the cycle, by (Q) the heat absorbed by the system, and by $(\int)$ an integral taken around the cycle. Thus

$$(W) = (\int) dW = (\int) pdV,$$
$$(Q) = (\int) dQ.$$

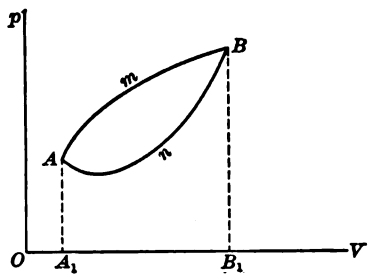


FIG. 2.

Let the point A, Fig. 2, represent the initial state of a system, and suppose that the system undergoes a cyclic transformation in passing to state B by the path m and returning from B to A by the path n. The work done *by* the system in changing from state A to state B along path m is represented by the area A_1AmBB_1, and the work done *on* the system by compression as the state changes from B back to A along path n is represented by the area B_1BnAA_1. Taking the first area as positive and the second as negative, the external work for the cycle is represented by the area $AmBnA$ enclosed by the curve of the cycle. That is, $(W) = (\int)pdV$ = area $AmBnA$.

If the cycle is traversed in the counter clockwise sense, that is, from A to B along path n and from B to A along path m, the integral $(\int)$ pdV is negative in sign and the area $AnBmA$ represents work done on the system.

Let us now consider the variation of the intrinsic energy U of the system during a cyclic transformation. The system originally in the state A has a definite amount of intrinsic energy made up of the thermal kinetic energy associated with the molecular

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velocity and indicated by the temperature, and thermal potential energy associated with the volume and state of aggregation. After passing through a series of changes, the system returns to the initial state A in which it has its initial temperature, volume, and state of aggregation. Consequently it must have the same intrinsic energy as at the beginning, and for the cycle the integral $(\int) dU$ reduces to zero.

As a corollary, we have the important result that the change of energy between states A and B is the same for paths m and n or for any other paths between the two points. For we have

$$(\int) dU = \int_{A}^{B}_{m} dU + \int_{B}^{A}_{n} dU = \int_{A}^{B}_{m} dU - \int_{A}^{B}_{n} dU = 0,$$

whence

$$\int_{A}^{B}_{m} dU = \int_{A}^{B}_{n} dU.$$

The change of energy between the states represented by points A and B depends only upon the points A and B and not at all upon the path between the points. In the initial state A the The energy is U_A determined by that state alone, and likewise in the second state B the system has a definite energy U_B which is fixed by the state. The change of energy between the states is therefore

$$\int_{A}^{B} dU = U_B - U_A.$$

The external work, on the other hand, for the change of state between points A and B, depends not only on the initial and final states but also on the character of the change, that is, on the path between points A and B. Thus the work done if the path n is followed is smaller than if path m is followed. We cannot associate numbers W_A and W_B with points A and B and obtain the work as the difference $W_B - W_A$; we may, however, denote the work by the symbol ${}_AW_B$, and write

$${}_AW_B = \int_{A}^{B} dW = \int_{V_a}^{V_b} p dV,$$

with the understanding that ${}_AW_B$ depends upon the path traversed and may be found when the path is known.

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Let the general energy equation be applied to the change of state. We have

$$J\int_A^B dQ = \int_A^B dU + \int_A^B dW,$$

or
$$J({}_AQ_B) = U_B - U_A + {}_AW_B. \tag{1}$$

Since the external work ${}_AW_B$ depends upon the path, it is evident that the heat absorbed in the process also depends on the path.

If the energy equation is applied to the closed cycle, the integration for the cycle gives

$$J(\int)dQ = (\int)dU + (\int)dW.$$

But since $(\int)\, dU = 0$, this equation reduces to

$$J(Q) = (W). \tag{2}$$

That is, *for a closed cycle the heat imparted to the system is the equivalent of the external work*, and both are represented graphically by the area of the cycle on the pV-plane.

20. Point Functions. Exact Differentials.—The intrinsic energy of a system, as has been shown, is determined by the state of the system; that is, it is a function of the coordinates that define the state. If the temperature and volume are chosen as the independent coordinates, we have, therefore,

$$u = f(t,\ v). \tag{1}$$

This means that for any substance there exists an equation that expresses u in terms of t and v. For example, it is found that for carbonic acid, the intrinsic energy is given by the expression

$$u = At - \frac{B}{v} + C, \tag{2}$$

in which A, B, and C are constants. The state of a system being represented graphically by a point in a plane, magnitudes like the intrinsic energy, which depend on the state only are called **point functions.** To find the change in a point function for a given change of state we have only to find the values of the function at the initial and final states and take the difference. Thus if the energy is expressed by (2), we have

$$u_1 = At_1 - \frac{B}{v_1} + C, \qquad u_2 = At_2 - \frac{B}{v_2} + C,$$

$$u_2 - u_1 = A(t_2 - t_1) + B\left(\frac{1}{v_1} - \frac{1}{v_2}\right).$$

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According to the rules of the differential calculus, the differentiation of (1) gives the expression

$$du = \frac{\partial u}{\partial t}\,dt + \frac{\partial u}{\partial v}\,dv, \tag{3}$$

which may be written

$$du = M dt + N dv, \tag{4}$$

M and N being the partial derivatives of u with respect to t and v.

Consider now q, the heat absorbed by the system, and W, the external work. For a change of state the path between the initial and final points must be known before the heat absorbed or the external work can be found. We cannot express q, therefore, as a function of the coordinates, that is, no such relation as

$$q = F(t,v)$$

exists. Nevertheless differential expressions of the form shown by (4) are permissible and have a definite meaning. We shall have occasion to make use of the relation

$$dq = M'dt + N'dv. \tag{5}$$

The differential expressions (4) and (5) have the same appearance but they are different in character. This difference appears in the interpretation of the coefficients M and M', N and N'. The coefficient M in (4) is the partial derivative of the function u with respect to the variable t and it expresses the rate of change of u with the temperature when the volume is held constant. The coefficient M' in (5) is the rate of absorption of heat with respect to the temperature, that is, the number of B. t. u. absorbed per degree rise in temperature with the volume constant, but it is not the partial derivative of a function because no such function exists. We may say that M and N in (4) are rates and also partial derivatives of a function; while M' and N' in (5) are likewise rates but *not* partial derivatives.

The differential expression $Mdt + Ndv$ in (4), which arises from the differentiation of a known function, is an **exact differential.** On the other hand a differential expression like $M'dt + N'dv$ in (5), which has no function lying back of it, and whose coefficients M' and N' are merely rates obtained by experiment, is called an **inexact differential.** If the differential

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is exact a certain relation must exist between the coefficients M and N, which are in this case partial derivatives of the function. Thus

$$M = \frac{\partial u}{\partial t}, \qquad N = \frac{\partial u}{\partial v},$$

$$\frac{\partial M}{\partial v} = \frac{\partial}{\partial v}\left(\frac{\partial u}{\partial t}\right) = \frac{\partial^2 u}{\partial v \partial t}, \qquad \frac{\partial N}{\partial t} = \frac{\partial}{\partial t}\left(\frac{\partial u}{\partial v}\right) = \frac{\partial^2 u}{\partial t \partial v};$$

hence

$$\frac{\partial M}{\partial v} = \frac{\partial N}{\partial t}. \tag{6}$$

The relation (6) furnishes a test of exactness which may be stated as follows; *Differentiate the first coefficient with respect to the second variable and the second coefficient with respect to the first variable. If the results are identical the differential is exact, otherwise it is inexact.*

The connection between point functions and exact differentials is obvious. The differential of any magnitude which, like the intrinsic energy, is a point function is exact. On the other hand, the differentials dq and dW of magnitudes that are not point functions are inexact.

As an example take the differential $v^n dp + npv^{n-1}dv$. $M = v^n$, $N = npv^{n-1}$, $\frac{\partial M}{\partial v} = nv^{n-1}$, $\frac{\partial N}{\partial p} = nv^{n-1}$. The differential is exact and is produced by differentiating the function pv^n. From the differential $vdp + npdv$, we obtain $\frac{\partial M}{\partial v} = \frac{\partial}{\partial v}(v) = 1$, $\frac{\partial N}{\partial p} = \frac{\partial}{\partial p}(np) = n$; hence the differential is inexact except when $n = 1$.

For the external work we have $dW = pdv + 0dp$. Applying the test, $\frac{\partial M}{\partial p} = \frac{\partial}{\partial p}(p) = 1$, $\frac{\partial N}{\partial v} = 0$; hence dW is inexact, and therefore the external work depends upon the path.

21. Adiabatic Processes.—When a system in changing its state has no thermal communication with other bodies and therefore neither absorbs nor gives out heat, the change of state is said to be **adiabatic.** In general, adiabatic changes are possible only when the system is inclosed in a non-conducting envelope. Rapid changes of state are approximately adiabatic, since time is required for conduction or radiation of heat; thus the alternate expansion and contraction of air during the passage of sound waves is nearly adiabatic; the flow of a gas or vapor through an orifice is practically an adiabatic process.

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For an adiabatic change from state 1 to state 2, the term ${}_1Q_2$ of the energy equation reduces to zero, and we have, consequently,

$$0 = U_2 - U_1 + {}_1W_2,$$

or

$${}_1W_2 = U_1 - U_2. \qquad (1)$$

During an adiabatic change, therefore, the external work done by the system is gained at the expense of the intrinsic energy of the system. Work done *on* the system adds to the intrinsic energy.

The projection on the pV-plane of the path of the state-point during an adiabatic change gives the adiabatic curve. See Fig. 3. The area A_1ABB_1 represents the work ${}_1W_2$ of the system and from (1) it represents also the decrease of the intrinsic energy in passing from state 1 represented by A to state 2 represented by B. Making use of this principle, we can arrive at a graphical representation of the intrinsic energy of a system. Suppose the adiabatic expansion to be continued indefinitely; the adiabatic curve AB will then approach the V-axis as an asymptote, and the work of the expanding system will be represented by the area $A_1A\infty$ between the ordinate A_1A, the axis OV, and the curve extended indefinitely. The area $A_1A\infty$ represents also the change of energy resulting from the expansion. Hence if we assume that the final energy is zero, we have

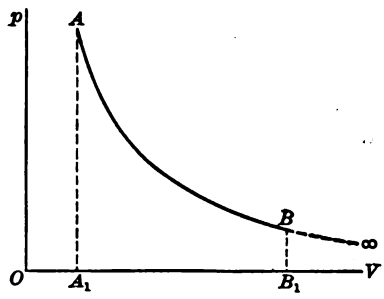


FIG. 3.

$$U_1 - 0 = \text{area } A_1A\infty,$$

or

$$U_1 = \text{area } A_1A\infty = \int_{V_1}^{\infty} pdV.$$

22. Effects of Heat on the Coordinates of the System.—As the result of absorption of heat the various coordinates of the system, pressure, volume and temperature, are, in general, changed. By the energy equation we expressed the heat absorbed in terms of the change of intrinsic energy and the external

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work done; we now attempt to express the heat absorbed in terms of the changes of the variables p, v and t.

Considering a unit weight of the substance, let dq denote the heat absorbed and let dp, dv, dt be the corresponding changes in p, v, and t, respectively. Then the quotients $\frac{dq}{dp}$, $\frac{dq}{dv}$, $\frac{dq}{dt}$ are the *rates* of absorption of heat with respect to the three variables; thus $\frac{dq}{dt}$ denotes the heat absorbed by one pound per degree rise in temperature. Evidently the heat absorbed is the product of the rate by the change of the variable; that is,

$$dq = \frac{dq}{dp}dp, \qquad dq = \frac{dq}{dv}dv, \qquad dq = \frac{dq}{dt}dt.$$

If the rate of absorption is known, the heat absorbed is obtained by integrating one of these expressions. For example, let $\gamma = \frac{dq}{dt}$ and suppose that for a given substance the value of γ has been determined by experiment; then

$$q = \int \gamma dt.$$

The term **thermal capacity** is applied to the heat required to change by one unit one of the coordinates p, v, t. The temperature is most frequently used as a measure of the heat supplied, and when used without qualification, the term thermal capacity refers to the heat absorbed by unit weight in raising the temperature one degree.

Since heat may have other effects than raising the temperature of the system, the value of the thermal capacity $\frac{dq}{dt}$ will depend on the conditions under which heat is absorbed. Two cases of special importance are: (1) The volume of the system is kept constant; (2) the pressure of the system is kept constant during the absorption of heat. The thermal capacities for these two cases are denoted, respectively, by

$$\gamma_v = \left(\frac{\partial q}{\partial t}\right)_v \qquad \text{and} \qquad \gamma_p = \left(\frac{\partial q}{\partial t}\right)_p.$$

For a solid or liquid γ_v and γ_p are practically identical, but in the case of a gas they are quite different.

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23. Specific Heat.—The **specific heat** of a substance at a given temperature t is the ratio of the thermal capacity of the substance at this temperature to the thermal capacity of an equal mass of water at some chosen standard temperature. If we take 17.5° C. (63.5° F.) as the standard temperature, and denote by γ thermal capacity per unit weight, then the specific heat c is given by the relation

$$c = \frac{\gamma_t(\text{of substance})}{\gamma_{17.5}(\text{of water})}. \tag{1}$$

But for water $\gamma_{17.5} = 1$ cal. It follows that the specific heat at the temperature t is numerically equal to the thermal capacity of unit weight at the same temperature: thus at 100° C. the thermal capacity of a gram of water is found to be 1.005 cal., and the specific heat is $\frac{\gamma_{100}}{\gamma_{17.5}} = \frac{1.005 \text{ cal}}{1 \text{ cal}} = 1.005$. Because of this numerical equality we shall hereafter use the single symbol c to denote either specific heat or thermal capacity.

If upon the absorption of heat the temperature of the system increases from t_1 to t_2, the quantity of heat absorbed is given by the equation

$$_1Q_2 = M\int_{t_1}^{t_2} c\,dt, \tag{2}$$

in which M denotes the weight and c the specific heat of the substance. If c is constant,

$$_1Q_2 = Mc(t_2 - t_1); \tag{3}$$

while if c is a linear function of the temperature, thus

$$c = c_0 + c_1 t, \tag{4}$$

we have

$$_1Q_2 = M\,[c_0\,(t_2 - t_1) + \tfrac{1}{2}\,c_1\,(t_2^2 - t_1^2]. \tag{5}$$

A system may consist of a mixture of substances, each having a definite thermal capacity or specific heat. The specific heat of the mixture may be found by an application of the principle that the heat absorbed by the mixture for a rise of temperature Δt is the same as the heat that would be absorbed by the separate constitituents for the same increase of temperature. Let

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M_1, M_2, M_3, . . . denote the weights and c_1, c_2, c_3, . . . the specific heat of the individual constituents: and let c denote the specific heat of the mixture. The heat absorbed by the mixture is

$$\Delta Q = (M_1 + M_2 + M_3 + ..)c\Delta t,$$

while the heat absorbed if the constituents are separated is

$$\Delta Q = (M_1c_1 + M_2c_2 + M_3c_3 + ..)\Delta t.$$

Equating the two expressions for ΔQ, the result is

$$c = \frac{M_1c_1 + M_2c_2 + M_3c_3 + \ldots}{M_1 + M_2 + M_3 + \ldots}. \qquad (6)$$

24. Latent Heat.—If the heat absorbed by a system is all expended in changing the state of aggregation, as in melting or vaporization, the temperature remains constant during the process and consequently the specific heat is infinite. In this case, the thermal coefficient $\left(\frac{\partial q}{\partial v}\right)_t$, the rate of absorption of heat with respect to the volume, is the important magnitude. This is denoted by l_v and is called the **latent heat of expansion.**

Let us consider the process of changing a unit weight of liquid at temperature t into vapor at the same temperature. The volume of unit weight of the liquid is denoted by v' and that of unit weight of the vapor by v''; and the heat absorbed in the process, called the latent heat of vaporization, is denoted by r. We have, therefore,

$$r = \left(\frac{\partial q}{\partial v}\right)_t (v'' - v') = l_v(v'' - v'). \qquad (1)$$

EXAMPLE. Water under a pressure of 118 lb. per sq. in. boils at a temperature of 340° F. and requires for vaporization 880.6 B. t. u. per lb. The volume of the steam formed is 3.796 cu. ft. per lb., that of the water 0.018 cu. ft. per lb. Hence the latent heat of expansion is

$$l_v = \frac{880.6}{3.796 - 0.018} = 235.7 \text{ B. t. u. per cu. ft.}$$

EXERCISES

1. If the thermal unit is taken as the heat required to raise the temperature of 1 pound of water from 17° to 18° C., what is the value of J in foot-pounds?

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2. In the combustion of a pound of coal 13,200 B. t. u. are liberated. If 7½ per cent of this heat is transformed into work in an engine, what is the coal consumption per horsepower-hour?

3. A gas engine is supplied with 11,200 B. t. u. per horsepower-hour. Find the percentage of the heat supplied that is transformed into work.

4. In a steam engine 193 B. t. u. of the heat brought into the cylinder by each pound of steam is transformed into work. Find the steam consumption per horsepower-hour.

5. A Diesel oil engine may under advantageous conditions transform as high as 38 per cent. of the heat supplied into work. If the combustion of a pound of oil develops 18,600 B. t. u., what weight of oil is required per h.p.-hr.?

6. From the expression for external work, ${}_1W_2 = \int_{V_1}^{V_2} pdV$, derive expressions for the work done when a gas expands from volume V_1 to volume V_2 (*a*) according to the law $pV = p_1V_1 = \text{const.}$; (*b*) according to the law $pV^n = p_1V_1^n = \text{const.}$

$$\text{Ans.} \begin{cases} (a)\ p_1V_1 \log_e \dfrac{V_2}{V_1} \\ (b)\ \dfrac{p_2V_2 - p_1V_1}{1 - n} \end{cases}$$

7. A gas while expanding does 14,800 ft.-lb. of work and at the same time receives from external sources 15 B. t. u. of heat. Is the energy increased or decreased, and how much?

8. In compressing air 34,000 ft.-lb. of work is expended and during the process water circulating in the surrounding jacket absorbs 12.5 B. t. u. Find the change of energy.

9. Determine which of the following differentials are exact and find the integrals of such as are exact.

(*a*) $vdp + npdv$

(*b*) $v^n dp + npv^{n-1}dv$

(*c*) $\dfrac{n(n+1)}{T^{n+1}}\ p(1 + 2ap^{\frac{1}{2}})dT - \dfrac{n+1}{T^n}\ (1 + 3ap^{\frac{1}{2}})dp.$

10. The differential $cdT + pdv$ (c a constant) is inexact. Show that $\dfrac{1}{T}$ is an integrating factor provided the relation $pv = BT$ is satisfied.

11. The energy u of a system is a point function of the coordinates, thus $u = f(t, v)$. Show that the energy equation ((3), Art. 20) may be written in the form

$$Jdq = \left(\frac{\partial u}{\partial t}\right)_v dt + \left[\left(\frac{\partial u}{\partial v}\right)_t + p\right] dv.$$

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12. From this equation derive the following:

(*a*) $\left(\frac{\partial u}{\partial T}\right)_v = Jc_v$.

(*b*) If the energy is independent of the volume, that is, if $\frac{\partial u}{\partial v} = 0$, then

$$Jdq = Jc_v dT + pdv.$$

13. Regnault's experiments on the heating of certain liquids are expressed by the following equations:

Ether	$q = 0.529t + 0.000296t^2$,	$-20°$ to $+30°$ C.
Chloroform	$q = 0.232t + 0.0000507t^2$,	$-30°$ to $+60°$ C.
Carbon disulphide	$q = 0.235t + 0.0000815t^2$,	$-30°$ to $+40°$ C.
Alcohol	$q = 0.5476t + 0.001122t^2 + 0.0000022\,t^3$,	$-23°$ to $+66°$ C.

From these equations derive expressions for the specific heat, and for each liquid find the specific heat at 20° C.

14. From the data of Ex. 13, find the mean heat capacity of ether between 0° and 30° C. Also the mean heat capacity of alcohol between 0° and 50° C.

15. If the thermal capacity of a substance at temperature t is given by the relation

$$\gamma = a + bt + ct^2,$$

show that the mean thermal capacity between 0° and t is given by the relation

$$\gamma_m = a + \tfrac{1}{2}\,bt + \tfrac{1}{3}\,ct^2.$$

16. Swann's experiments on the specific heat of air at constant pressure are represented by the equation $c_p = 0.2413\ (1 + 0.00005t)$, in which t denotes temperature on the C. scale. Find the heat required to raise the temperature of 18 lb. of air from 20° C. to 95° C. Ans. 588 B. t. u

17. For the specific heat of carbon dioxide at constant pressure the following equation has been suggested: $c_p = 0.1991 + 8.73 \times 10^{-4}t - 23.4 \times 10^{-8}t^2 + 12.8 \times 10^{-11}t^3$; t denotes temperature on the F. scale. Find the heat absorbed by 5 lb. of CO_2 at constant pressure when the temperature is increased from 200° F. to 2700° F. Ans. 4079.6 B. t. u.

18. Water at 32° F. weighs 62.42 lb. per cu. ft. and ice weighs 57.2 lb. per cu. ft. Find the external work done when 1 lb. of ice is melted under atmospheric pressure.

19. In a boiler water is vaporized under a constant pressure of 150 lb. per sq in. The volume of 1 lb. of the steam formed is 3.02 cu. ft., the volume of 1 lb. of water is 0.018. Find the heat required to perform the work of expansion against the constant pressure. Ans. 83.3 B. t. u.

20. The heat required for vaporization in Ex. 19 is 864.9 B. t. u. In what way is the remaining 781.6 B. t. u. expended?

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21. The metric horsepower is defined as 75 kilogram-meters of work per second. Find the equivalent in kilogram-calories of a metric horsepower-hour.

22. Find the numerical relations between the following energy units:

(*a*) Joule and B. t. u.
(*b*) Joule and metric h.p.-hr.
(*c*) B. t. u. and kg.-meter.
(*d*) h.p.-minute and B. t. u.

23. A unit of power is the watt, which is defined as 1 joule per second. 1 kilowatt (kw.) is 1000 watts. Find the number of B. t. u. in a kw.-hr.; the number of foot-pounds in a watt-hour.

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CHAPTER III

PROPERTIES OF GASES

25. The Permanent Gases.—The term "permanent gas" survives from an earlier period, when it was applied to a series of gaseous substances which supposedly could not by any means be changed into the liquid or solid state. The recent experimental researches of Pictet and Cailletet, of Wroblewski, Olszewski, and others have shown that, in this sense of the term, there are no permanent gases. At sufficiently low temperatures all known gases can be reduced to the liquid state. The following are the temperatures of liquefaction of the more common gases at atmospheric pressure:

Atmospheric air	−192.2° C.
Nitrogen	−193.1° C.
Oxygen	−182.5° C.
Hydrogen	−252.5° C.
Helium	−263.9° C.

It appears, therefore, that the so-called permanent gases are in reality superheated vapors far removed from temperature of condensation. We shall understand the term "permanent gas" to mean, therefore, a gas that is liquefied with difficulty and that obeys very closely the Boyle-Gay Lussac law. Gases that show considerable deviations from this law because they lie relatively near the condensation limit will be known as superheated vapors

26. Boyle's Law.—At moderate pressures the permanent gases obey quite exactly Boyle's law, namely:

If the temperature is kept constant, the volume of a given weight of gas varies inversely as the temperature.

This law is expressed symbolically by the equation

$$pv = C, \tag{1}$$

or

$$p_1v_1 = p_2v_2 = p_3v_3 = \ldots \tag{2}$$

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A change of state at constant temperature is called an **isothermal** change. On the pv-plane the curves representing isothermal changes of a gas are given by equation (1); therefore they are equilateral hyperbolas.

27. Charles' Law.—According to the law of Charles, *the increase of pressure when the gas is heated at constant volume is proportional to the increase of temperature;* that is,

$$p - p_0 = k(t - t_0). \tag{1}$$

This equation defines, in fact, the scale of the constant volume gas thermometer. Charles' law is shown graphically in Fig. 4. Point A represents the initial condition (p_0, t_0), point B the final condition (p, t). Then

$$CB = p - p_0, \quad AC = t - t_0, \quad \text{and} \quad \frac{CB}{AC} = \frac{p - p_0}{t - t_0} = k.$$

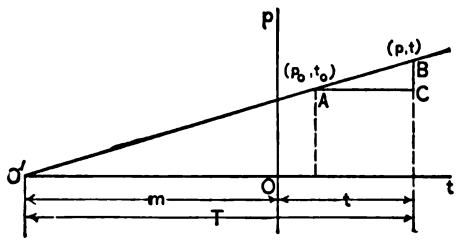


FIG. 4.

According to Charles' law, therefore, the points representing the successive values of p and t, with v constant, lie on a straight line through the initial point A, and the slope of this line is the constant k.

Conceive the line through A and B prolonged to intersect the t-axis at the point O', and let m denote the length $O'O$. Suppose that the origin be shifted from O to O' and that temperatures measured from O' be denoted by T instead of t. At point B, for example, t denotes the temperature measured from origin O, T the temperature measured from origin O', and $T = t + m$. Since the slope of the line AB is the constant k, we have

$$p = kT, \qquad p_0 = kT_0,$$

or

$$p_0/p = T_0/T; \tag{2}$$

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that is, at constant volume, the pressure of the gas is proportional to its temperature measured from the new origin O'.

28. Absolute Temperature.—The zero of temperature indicated by the origin O', Fig. 4, is called the **absolute zero,** and temperatures taken from it are called **absolute** temperatures. Assuming that the change of state of the gas at constant volume can be represented by the straight line BA until O' is reached, the point O' represents a state in which the pressure is zero. According to the kinetic theory the pressure of a gas is due to the impact of molecules on the walls of the containing vessel; therefore zero pressure indicates a state in which molecular motion of translation has ceased.

The position of the absolute zero relative to the centigrade zero may be determined approximately by experiment on the nearly perfect gases, as air, nitrogen or hydrogen.

Let T_0 be taken as the absolute temperature of melting ice, T_1 that of boiling water at atmospheric pressure. Regnault's experiments on the increase of pressure of air when heated at constant volume gave the relation

$$\frac{p_1(\text{at } 100^\circ \text{ C.})}{p_0(\text{at } 0^\circ \text{ C.})} = 1.3665. \tag{1}$$

We have therefore

$$T_0 = \frac{100}{0.3665} = 272.85; \tag{2}$$

that is, using air as the thermometric substance, the absolute zero is 272.85°C. below the temperature of melting ice. Other approximately perfect gases, as nitrogen, hydrogen, etc., give slightly different values for T_0. The experiments of Joule and Thomson indicate that for an ideal perfect gas the value of T_0 lies between 273.1 and 273.14. The corresponding value on the Fahrenheit scale may be taken as 491.6: that is, the absolute zero is 491.6° below the temperature of melting ice, or 459.6° below the ordinary F. zero. Hence

for the C scale	$T = t + 273.1;$
for the F scale	$T = t + 459.6.$

29. Characteristic Equation.—Combination of the laws of Boyle and Charles gives a relation between p, v, and t, which is

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the characteristic equation of a gas. The two laws are expressed symbolically as follows;

Boyle's law, $pv = C'$ when T is constant;

Charles' law, $\frac{p}{T} = C''$ when v is constant.

Evidently the single relation that satisfies these two conditions is

$$\frac{pv}{T} = \text{const.} \tag{1}$$

The constant in this equation is denoted by the symbol B; and the equation is usually given the form

$$pv = BT. \tag{2}$$

Let M denote the weight of gas under consideration; then the volume is $V = Mv$, and from (2) we have

$$p(Mv) = MBT$$

or

$$pV = MBT, \tag{3}$$

a form of the equation that is frequently useful.

The homogeneous form of the characteristic equation is advantageous in the solution of problems that involve two states of the gas. If (p_1, V_1, T_1) and $(p_2, V_2 T_2)$ are the two states in question, then

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}. \tag{4}$$

With this equation any consistent system of units may be used.

EXAMPLE. Air at a pressure of 14.7 lb. per square inch and having a temperature of 60° F. is compressed from a volume of 4 cu. ft. to a volume of 1.35 cu. ft. and the final pressure is 55 lb. per square inch. The final temperature is to be found.

From (4) we have

$$\frac{14.7 \times 4}{60 + 459.6} = \frac{55 \times 1.35}{t_2 + 459.6}$$

whence $t_2 = 196.5°$ F.

Any characteristic equation, $v = f(p, T)$, having three variables, may be represented geometrically by a surface. A state of the system is defined by the coördinates p, v, T, and this state is

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therefore represented by a point on the surface. A change of state is represented by the movement of the state-point on the surface.

The surface that represents the characteristic equation $pv = BT$ is shown in Fig. 5. A plane perpendicular to the T-axis cuts the surface in an equilateral hyperbola, whose equation is $pv = \text{const.}$ Making v constant the equation becomes

$$p = \frac{B}{v} T = C_1 T;$$

hence a plane perpendicular to the V-axis cuts the surface in a straight line given by this last equation.

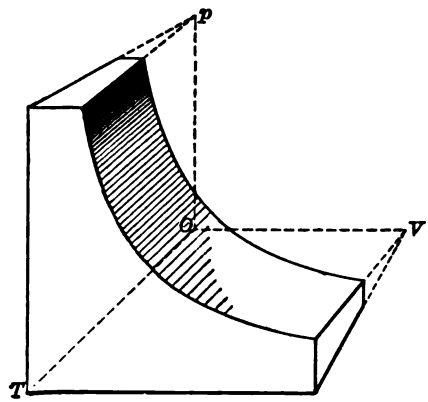


FIG. 5.

30. Numerical Value of B.—The value of the constant B for a given gas can be determined from the values of p, v, and T belonging to some definite state. The specific weights of various gases at atmospheric pressure and at a temperature of 0° C. are as follows:[1]

Air	0.08071	lb. per cubic foot.
Nitrogen	0.07812	lb. per cubic foot.
Oxygen	0.08922	lb. per cubic foot.
Hydrogen	0.005621	lb. per cubic foot.
Carbonic acid	0.12341	lb. per cubic foot.

[1] Smithsonian Physical Tables, 6th Ed., p. 91.

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A pressure of one atmosphere, 760 mm. of mercury, is 10,333 kg. per square meter = 14.6966 lb. per square inch = 2116.31 lb. per square foot. Taking 491.6 as the value of T on the F. scale corresponding to 0° C., we have for air

$$B = \frac{pv}{T} = \frac{p}{\gamma T} = \frac{2116.31}{0.08071 \times 491.6} = 53.34.$$

In metric units the corresponding calculation gives

$$B = \frac{10333}{273.1 \times 1.293} = 29.26.$$

The values of B for other gases may be found in the same way by inserting the proper values of the specific weight γ.

31. Joule's Law.—By an application of the laws of thermodynamics it may be shown that if a gas strictly obeys the laws of Boyle and Charles it must also obey a third law, which may be stated as follows:

The intrinsic energy of a perfect gas depends upon the temperature only, and is independent of the volume.

This law may be stated symbolically by the relations

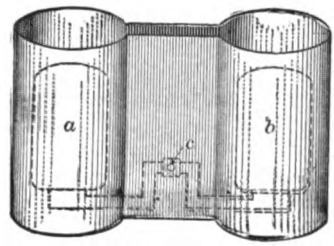


FIG. 6.

$$u = f(t), \quad \frac{\partial u}{\partial v} = 0.$$

That the law holds, at least approximately, in the case of actual gases was first established experimentally by Joule. The apparatus used is shown in Fig. 6. Two vessels a and b connected by a tube were immersed in a bath of water. In one vessel air was compressed to a pressure of 22 atmospheres, the other vessel was exhausted. The temperature of the water was taken by a very sensitive thermometer. A stopcock c in the connecting tube was then opened, permitting the air to rush from a to b, and after equilibrium was established the temperature of the water was again read. No change of temperature could be detected.

From the conditions of the experiment no work external to the vessels a and b was done by the gas; and since the water

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remained at the same temperature, no heat passed into the gas from the water. Consequently, the internal energy of the air was the same after the expansion into the vessel b as before. Now if the increase of volume had required the expenditure of internal work, *i.e.* work to force the molecules apart against their mutual attractions, that work must necessarily have come from the internal kinetic energy of the gas, and as a result the temperature would have been lowered. As the temperature remained constant, it is to be inferred that no such internal work was required. A gas has, therefore, no appreciable internal potential energy; its energy is entirely kinetic and depends upon the temperature only.

The more accurate porous-plug experiments of Joule and Lord Kelvin showed that all gases deviate more or less from Joule's law. In the case of the so-called permanent gases, air, hydrogen, etc., the deviation was slight though measurable; but with the gases more easily liquefied, the deviations were more marked. The explanation of these deviations is not difficult when the true nature of a gas is considered. Presumably the molecules of a gas act on each other with certain forces, the magnitudes of which depend upon the distances between the molecules. When the gas is highly rarefied, that is, when it is far removed from the liquid state, the molecular forces are vanishingly small; but when the gas is brought nearer the liquid state by increasing the pressure and lowering the temperature, the molecules are brought closer together and the molecular forces are no longer negligible. The gas in this state possesses appreciable potential energy and the deviation from Joule's law is considerable.

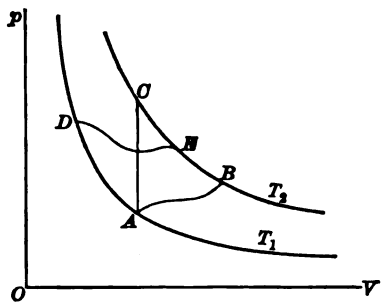


FIG. 7.

32. Energy Equation for a Gas.—Let T_1 and T_2, Fig. 7, be two isothermal curves drawn on the pV-plane. According to Joule's law, the energy being fixed by the temperature is the the same at all points, as A and D, on T_1; likewise the energy

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at all points on T_2, as B, E, and C, has the same value u_2. It follows that the change of energy $u_2 - u_1$ in passing from the isothermal T_1 to the isothermal T_2 is the same by all paths. That is, if the change $u_2 - u_1$ can be found for the path AC, it is likewise the change for paths AB and DE.

The path AC represents an increase of temperature of constant volume. Taking the general energy equation

$$Jdq = du + pdv, \tag{1}$$

we have for this path, since v is constant and $dv = 0$,

$$Jdq = du. \tag{2}$$

But if c_v is the specific heat at constant volume, we have also from the specific heat equation

$$dq = c_v dT. \tag{3}$$

Therefore, combining (2) and (3)

$$du = Jdq = Jc_v dT \tag{4}$$

whence

$$u_2 - u_1 = Jc_v(T_2 - T_1), \tag{5}$$

provided c_v is constant.

Equation (5) gives the change of energy for the constant volume path AC, but the change is the same for other paths as AB or DE. Therefore (5) is a general expression for the change of energy of a gas when the temperature is changed from T_1 to T_2 under any condition whatever.

If in the general equation (1) the expression for du given in (4) is substituted the result is

$$Jdq = Jc_v dT + pdv, \tag{6}$$

or

$$dq = c_v dT + Apdv. \tag{7}$$

Equation (7) is the fundamental energy equation of gases.

33. Relation between c_p and c_v.—The heat absorbed by a gas under the condition that the pressure remain constant is obtained from the equation

$$dq = c_p dT, \tag{1}$$

in which c_p denotes the specific heat at constant pressure. It is

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evident that c_p must be larger than c_v, for the reason that in the case of a change at constant pressure external work is done, and additional heat must be supplied for the performance of this work. The relation betwen the two specific heats may be established as follows. From the characterisitc equation

$$pv = BT, \tag{2}$$

we have with p constant

$$pdv = BdT. \tag{3}$$

Hence the energy equation (7) of the preceding article takes the form

$$\begin{aligned} dq &= c_v\, dT + ABdT \\ &= (c_v + AB)\, dT \end{aligned} \tag{4}$$

when the pressure is constant. Now combining (1) and (4), we have the important relation

$$c_p = c_v + AB,$$

or

$$c_p - c_v = AB. \tag{5}$$

The ratio c_p/c_v is denoted by the symbol k; that is

$$c_p = kc_v, \qquad c_v = \frac{c_p}{k}. \tag{6}$$

Introducing the ratio k in (5), we obtain the relations

$$c_v = \frac{AB}{k-1}, \qquad c_p = \frac{kAB}{k-1}. \tag{7}$$

The specific heats c_p and c_v of most gases are found to increase slowly with the temperature. If the temperature range is not too large it is, however, permissible to assume constant mean values. In this chapter we shall take the specific heats as constant, and in a subsequent chapter deal with problems that involve variable specific heats.

The following table gives mean values of c_p, c_v, and k for several gases.

Gas	c_p	c_v	k
Air	0.242	0.173	1.40
Hydrogen	3.410	2.420	1.41
Nitrogen	0.244	0.173	1.41
Oxygen	0.224	0.160	1.40
Carbon monoxide	0.243	0.174	1.40
Carbon dioxide	0.203	0.156	1.30

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34. Intrinsic Energy of a Gas.—From equation (4) of Art. 32, namely

$$du = Jc_v dT, \tag{1}$$

we obtain by integration the general expression

$$u = J\int c_v dT, \tag{2}$$

and if c_v is constant,

$$u = Jc_v T + u_0, \tag{3}$$

in which u_0 is a constant of integration. The absolute value of u_0 for any gas is unknown, and in the case of most investigations it is of no importance because *changes* of energy are required and the constant disappears upon subtraction. However, it must not be assumed that the value of the constant may be taken as zero; in certain investigations of gas mixtures this constant plays an important part.

For a weight of M pounds of gas the energy is

$$U = JMc_v T + U_0, \tag{4}$$

where $U_0 = Mu_0$. This formula may be given another form that is usually more convenient for practical use. Multiply and divide by B, and write $J = \frac{1}{A}$; then (4) becomes

$$U = \frac{c_v}{AB} MBT + U_0.$$

But $MBT = pV$, and $\frac{c_v}{AB} = \frac{1}{k-1}$ (See (7), Art. 33). Therefore

$$U = \frac{pV}{k-1} + U_0. \tag{5}$$

If the gas passes from an initial state (p_1, v_1, t_1) to a second state (p_2, v_2, t_2) the change of energy is

$$U_2 - U_1 = \frac{p_2V_2 - p_1V_1}{k-1}. \tag{6}$$

In this formula V_2 and V_1 denote the final and initial volumes, respectively, of the weight of gas under consideration; consequently it is not necessary to find the weight M in order to calculate the change of energy. It is to be noted, however, that in, using (6) pressures must be taken in pounds per square *foot*.

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EXAMPLE. Find the change of energy when 8.2 cu. ft. of air having a pressure of 20 lb. per square inch is compressed to a pressure of 55 lb. per square inch and a volume of 3.72 cu. ft.

Using the value $k = 1.40$,

$$U_2 - U_1 = 144 \times \frac{55 \times 3.72 - 20 \times 8.2}{0.40} = 14{,}616 \text{ ft. lb.}$$

35. Isothermal Change of State.—If T is made constant in the equation $pV = MBT$, the resulting equation

$$pV = p_1V_1 = \text{constant} \tag{1}$$

is the equation of the isothermal curve in pV-coördinates. This curve is an equilateral hyperbola. The external work for a change from state 1 to state 2 is given by the general formula

$${}_1W_2 = \int_{V_1}^{V_2} p dV. \tag{2}$$

Using (1) to eliminate p, we have

$${}_1W_2 = p_1V_1 \int_{V_1}^{V_2} \frac{dV}{V} = p_1V_1 \log_e \frac{V_2}{V_1}$$

$$= MBT \log_e \frac{V_2}{V_1}. \tag{3}$$

For the change of energy,

$$U_2 - U_1 = JMc_v(T_2 - T_1) = 0; \tag{4}$$

hence

$${}_1Q_2 = A_1W_2 = Ap_1V_1 \log_e \frac{V_2}{V_1}. \tag{5}$$

Since in isothermal expansion the work done is wholly supplied by the heat absorbed from external sources, it follows that if the expansion is continued indefinitely, the work that may be obtained is infinite. This is also shown by (3); thus

$$p_1V_1 \int_{V_1}^{\infty} \frac{dV}{V} = p_1V_1 \log_e \frac{\infty}{V_1} = \infty. \tag{6}$$

36. Adiabatic Changes.—(*a*) *Relations between the coördinates.* The energy equation for a gas, namely

$$dq = c_v dT + Apdv, \tag{1}$$

applies to all changes of state. In an adiabatic process no heat

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is supplied to or taken from the system, that is, $dq = 0$. Therefore for an adiabatic change (1) takes the form

$$c_v dT + Apdv = 0. \tag{2}$$

If this equation is combined with the characteristic equation

$$pv = BT \tag{3}$$

one of the three variables may be eliminated and the equation remaining will give the relation between the other two. To get the adiabatic curve on the pv-plane the variable T should be eliminated.

Differentiating (3) and multiplying through by A, we obtain

$$Avdp + Apdv = ABdT = (c_p - c_v)dT = (k - 1)c_v dT \tag{4}$$

or, taking account of (2),

$$Avdp + Apdv + (k - 1)Apdv = 0,$$

which reduces to

$$vdp + kpdv = 0. \tag{5}$$

Integration of this equation gives the desired relation between p and v. Separating the variables, we have

$$\frac{dp}{p} + k\frac{dv}{v} = 0,$$

whence

$$\log p + \log v^k = \log C,$$

or

$$pv^k = C. \tag{6}$$

The relation between temperature and volume or between temperature and pressure is readily derived by combining (6) and the general equation $pv = BT$. Thus from

$$pv^k = C,$$

$$pv = BT,$$

we get by the elimination of p

$$v^{k-1} = \frac{C}{BT};$$

that is,

$$Tv^{k-1} = \text{const.} \tag{7}$$

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Similarly, by the elimination of v we obtain

$$p^{k-1} = \frac{B^k}{C} T^k;$$

that is,

$$\frac{p^{\frac{k-1}{k}}}{T} = \text{const.} \tag{8}$$

If we choose some initial state, p_1, v_1, T_1, the constants in (7) and (8) are determined, and the equations may be written in the homogeneous forms

$$\frac{T}{T_1} = \left(\frac{v_1}{v}\right)^{k-1} = \left(\frac{p}{p_1}\right)^{\frac{k-1}{k}}. \tag{9}$$

(*b*) *External Work.*—In an adiabatic change the heat absorbed is zero and the energy equation becomes

$${}_1W_2 = -(U_2 - U_1) = U_1 - U_2.$$

Using the general expression for the change of energy,

$${}_1W_2 = \frac{p_1V_1 - p_2V_2}{k - 1}. \tag{10}$$

By means of the equation

$$p_1V_1^k = p_2V_2^k,$$

the final volume V_2 may be eliminated from (10). The resulting equation is

$${}_1W_2 = \frac{p_1V_1}{k - 1}\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right]. \tag{11}$$

EXAMPLE. An air compressor compresses adiabatically 1.2 cu. ft. of free air (*i.e.*, air at atmospheric pressure, 14.7 lb. per square inch) to a pressure of 70 lb. per square inch. Find the work of compression; also the final temperature if the initial temperature is 60° F.

$$V_2 = 1.2\left(\frac{14.7}{70}\right)^{\frac{1}{1.4}} = 0.3936 \text{ cu. ft.}$$

The work of compression is

$$\frac{p_1V_1 - p_2V_2}{k - 1} = \frac{144(14.7 \times 1.2 - 70 \times 0.3936)}{0.4} = -3568 \text{ ft.-lb.}$$

The initial temperature being 60° + 459.6° = 519.6° absolute, we have for the final temperature

$$T_2 = 519.6\left(\frac{70}{14.7}\right)^{\frac{0.4}{1.4}} = 811.6 \text{ abs.},$$

whence $t_2 = 352°$ F.

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(c) *Comparison of Adiabatics and Isothermals.*—The equations of the adiabatic and isothermal curves in pv coordinates are, respectively,

$$pv^k = C_1, \qquad pv = C_2.$$

Therefore the two curves must intersect, as at point A, Fig. 8. Since the exponent k is always greater than 1, it follows that the steeper curve AB' must be the adiabatic. A physical explanation is afforded by the fact that during the adiabatic expansion from A to B' external work represented by the area $A_1AB'B_1$ is done at the expense of the initial energy of the gas. Hence for the same final volume, the temperature, and consequently the pressure, is lower for the adiabatic than for the isothermal curve.

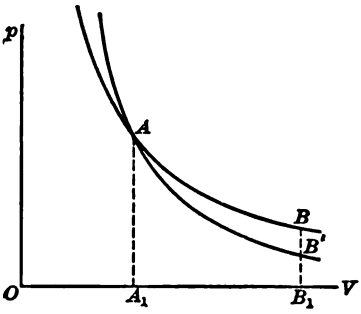


FIG. 8.

If the two curves are produced indefinitely, each will have the axis OV as an asymptote. The area under the indefinitely extended isothermal (Eq. (6), Art. 35) is infinite; on the other hand, the area under the adiabatic must be finite because the work that can be obtained in an adiabatic expansion cannot exceed the initial intrinsic energy in the system The maximum work may be found by making $p_2 = 0$ in (11), thus

$$W_{max} = \frac{p_1V_1}{k - 1}.$$

37. Polytropic Changes of State.—In the practical examples of expansion or compression of gases, as the compression of air or the expansion of products of combustion in the gas engine, the pv-curve for the change of state follows, at least approximately, the equation

$$pv^n = \text{const.} \qquad (1)$$

The curve that represents this equation is called the **polytropic** curve.

By giving n special values we get the constant volume, constant pressure, and other familiar changes of state. Thus:

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for $n = 0$, $pv^0 = \text{const.}$, *i.e.*, $p = \text{const.}$

for $n = \infty$, $p^{\frac{1}{\infty}}v = \text{const.}$, $v = \text{const.}$

for $n = 1$, $pv = \text{const.}$, isothermal.

for $n = k$, $pv^k = \text{const.}$, adiabatic

By combining (1) with the characteristic equation $pV = MBT$, as in Art. 36, the following relations are readily derived.

$$\frac{T}{T_1} = \left(\frac{V_1}{V}\right)^{n-1} = \left(\frac{p}{p_1}\right)^{\frac{n-1}{n}}. \tag{2}$$

For the external work done by a gas expanding according to the law $pV^n = p_1V_1^n = \text{const.}$ from the volume V_1 to the volume V_2, we have

$$\begin{aligned} {}_1W_2 &= \int_{V_1}^{V_2} p\,dV = p_1V_1^n \int_{V_1}^{V_2} V^{-n}dV \\ &= p_1V_1^n\left[\frac{V_2^{1-n} - V_1^{1-n}}{1-n}\right] \\ &= \frac{p_2V_2 - p_1V_1}{1-n}. \end{aligned} \tag{3}$$

The change of energy, as in every change of state, is

$$U_2 - U_1 = \frac{p_2V_2 - p_1V_1}{k-1}. \tag{4}$$

Hence, from the energy equation, we have for the heat absorbed by the gas during expansion

$$J_1Q_2 = U_2 - U_1 + {}_1W_2 = \frac{p_2V_2 - p_1V_1}{k-1} + \frac{p_2V_2 - p_1V_1}{1-n}$$

or $$J_1Q_2 = \frac{k-n}{(k-1)(1-n)}(p_2V_2 - p_1V_1). \tag{5}$$

Comparing (3), (4), and (5), it is seen that the common factor $(p_2V_2 - p_1V_1)$ occurs in the second member of each expression. Hence, dropping out this factor, we may write the following useful relations:

$$\frac{W}{U_2 - U_1} = \frac{k-1}{1-n}, \tag{6}$$

$$\frac{W}{JQ} = \frac{k-1}{k-n}, \tag{7}$$

$$\frac{JQ}{U_2 - U_1} = \frac{k-n}{1-n}. \tag{8}$$

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These may be combined in the one expression

$$W : U_2 - U_1 : JQ = k - 1 : 1 - n : k - n. \tag{9}$$

EXAMPLE. Let a gas expand according to the law

$$pV^{1.2} = \text{const.}$$

Taking $k = 1.4$, we have

$$W : U_2 - U_1 : JQ = 0.4 : -0.2 : 0.2 = 2 : -1 : 1;$$

that is, the external work is double the equivalent of the heat absorbed by the gas and also double the *decrease* of energy.

38. Specific Heat in Polytropic Changes.—From (5), Art. 37, an expression for ${}_1Q_2$ in terms of the initial and final temperatures of the gas may be readily derived. Since

$$p_1V_1 = MBT_1, \text{ and } p_2V_2 = MBT_2,$$

(5) becomes

$${}_1Q_2 = \frac{MAB}{k-1}\frac{k-n}{1-n}(T_2 - T_1).$$

But $$\frac{AB}{k-1} = c_v;$$

hence $${}_1Q_2 = Mc_v\frac{k-n}{1-n}(T_2 - T_1). \tag{1}$$

We have, in general,

$${}_1Q_2 = Mc_n(T_2 - T_1), \tag{2}$$

where c_n denotes the specific heat for the change of state under consideration. Comparing (1) and (2), it appears that

$$c_n = c_v\frac{k-n}{1-n}. \tag{3}$$

Hence, for the polytropic change of state, *the specific heat is constant* (assuming c_v to be constant) and its value depends on the value of n in the equation $pV^n = \text{const.}$

It is instructive to observe from (3) the variation of c_n as n is given different values. For $n = 0$, $c_n = kc_v = c_p$, and the change of state is represented by the constant-pressure line *aa*, Fig. 9. For $n = 1$, $c_n = \infty$, and the change of state is isothermal (line *b*). If $n = k$, then $c_n = 0$, and the expansion is adiabatic (line *d*). For values of n lying between 1 and k, the value of c_n as given by (3) is evidently negative; that is, for any curve lying between the isothermal *b* and adiabatic *d*, rise of tempera-

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ture accompanies abstraction of heat, and *vice versa*. This is shown by the curve *c*.

39. Determination of the Exponent *n*.—It is frequently desirable in experimental investigation to fit a curve determined experimentally —as, for example, the compression curve of the indicator diagram of the air compressor—by a theoretical curve having the general equation $pV^n = c$. To find the value of the exponent n we assume two points on the curve and measure to any convenient scale p_1, p_2, V_1, and V_2. Then since

$$p_1 V_1^n = p_2 V_2^n,$$

we have

$$n = \frac{\log p_2 - \log p_1}{\log V_1 - \log V_2}. \qquad (1)$$

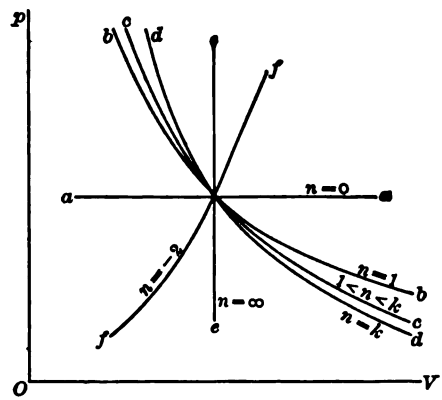


FIG. 9.

EXAMPLE. In a test of an air compressor the following data were determined from the indicator diagram:

At the beginning of compression, $p_1 = 14.5$ lb. per square inch.
$V_1 = 2.56$ cu. ft.
At the end of compression, $p_2 = 68.7$ lb. per square inch.
$V_2 = 0.77$ cu. ft.

Assuming that the compression follows the law $pV^n = \text{const.}$, we have for the value of the exponent

$$n = \frac{\log 68.7 - \log 14.5}{\log 2.56 - \log 0.77} = 1.32.$$

The work of compression is

$${}_1W_2 = \frac{p_2V_2 - p_1V_1}{1 - n} = \frac{144(68.7 \times 0.77 - 15.5 \times 2.56)}{-0.32} = -7100 \text{ ft.-lb.}$$

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The increase of intrinsic energy is

$$U_2 - U_1 = \frac{p_2V_2 - p_1V_1}{k-1} = \frac{144\,(68.7 \times 0.77 - 14.5 \times 2.56)}{0.4} = 5680 \text{ ft-lb.};$$

and the heat absorbed is

$${}_1Q_2 = \frac{5680 - 7100}{778} = -1.83 \text{ B.t.u.}$$

The negative sign indicates that heat is given up by the air during compression; this is always the case with a water-jacketed cylinder.

If the initial temperature of the air is 60° F., or 519.6° absolute, the final temperature is

$$T_2 = 519.6\left(\frac{2.56}{0.77}\right)^{0.32} = 763.2,$$

whence $t_2 = 303.6°$ F.

EXERCISES

1. Find values of the constant B for nitrogen, oxygen, and hydrogen.

2. Establish a relation between the density of a gas and the value of the constant B for that gas.

3. Find the volume of 13 lb. of air at a pressure of 85 lb. per square inch and a temperature of 72° C. Ans. 35.19 cu. ft.

4. If the air in Ex. 3 expands to a volume of 130 cu. ft. and the final pressure is 20 lb. per square inch, what is the final temperature? Ans. 26.9° C.

5. What weight of hydrogen at atmospheric pressure and a temperature of 70° F. will be required to fill a balloon having a capacity of 20,000 cu. ft.? Ans. 104.3 lb.

6. A gas tank contains 2.1 lb. of oxygen at a pressure of 120 lb. per square inch and at a temperature of 60° F. The pressure in the tank should not exceed 300 lb. per square inch and the temperature may rise to 100° F. Find the weight of oxygen that may safely be added to the contents of the tank. Ans. 2.775 lb.

7. The volume of a fire balloon is 120 cu. ft. The air inside has a temperature of 280° F., and the temperature of the surrounding air is 70° F. Find the weight required to prevent the balloon from ascending, including the weight of the balloon itself. Ans. 2.55 lb.

8. A tank having a volume of 35 cu. ft. contains air compressed to 90 lb. per square inch absolute. The temperature is 70° F. Some of the air is permitted to escape, and the pressure in the tank is then found to be 63 lb. per square inch and the temperature 67° F. Find the volume occupied by the air removed from the tank at atmospheric pressure and at 70° F. Ans. 63.43 lb.

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9. Air changes state according to the law $pV^n = C$. Find the value of n for which the decrease of energy is one-half of the external work; also the value of n for which the heat abstracted is one-third of the increase of energy.

Ans. 1.2; 1.3.

10. If 32,000 ft.-lb. are expended in compressing air according to the law $pV^{1.28} = \text{const.}$, find the heat abstracted, and the change of energy.

11. In heating air at constant pressure the heat absorbed is 350 B. t. u. Find the increase of energy and the external work.

12. A mass of air at a pressure of 60 lb. per square inch absolute has a volume of 12 cu. ft. The air expands to a volume of 20 cu. ft. Find the external work and change of energy: (*a*) when the expansion is isothermal; (*b*) when the expansi n is adiabatic; (*c*) when the air expands at constant pressure.

Ans. $\begin{cases} (a)\ W = 52{,}960 \text{ ft.-lb.} \\ (b)\ W = 47{,}900 \text{ ft.-lb.} \\ (c)\ W = 69{,}120 \text{ ft.-lb.} \end{cases}$

13. Air in the initial state has a volume of 8 cu. ft. at a pressure of 75 lb. per square inch. In the final state the volume is 18 cu. ft. and the pressure is 38 lb. per square inch. Find the change of energy.

14. Find the work required to compress 50 cu. ft. air from a pressure of 14.7 lb. to a pressure of 125 lb. per square inch, according to the law $pv^{1.3} = \text{const.}$ Find the heat abstracted during compression.

Ans. 225,200 ft.-lb.; 72.4 B. t. u.

15. Air at atmospheric pressure is compressed to a pressure of 105 lb. per sq. in. according to the law $pv^n = \text{const.}$ The initial temperature is 60° F. Take n = 1.0, 1.1, 1.2, 1.3, 1.4 and for each value calculate the final temperature and the heat rejected per pound.

16. Find the decrease of intrinsic energy when 34 lb. of air is cooled from 225° F. to 65° F. Ans. 94.11 B. t. u.

17. The change of state follows the law $pv^n = \text{const.}$ Fill in the vacant spaces in the following.

	n	t_1	t_2	p_1	p_2	V_1	V_2
(*a*)	1.25	60°	—	15	95	6.4	—
(*b*)	1.31	255°	—	120	—	30	110
(*c*)	1.0	—	85°	—	20	15	45
(*d*)	—	—	190°	14	88	35	7

18. Air is cooled at a constant pressure of 60 lb. per sq. in. from 110° to 60° F. The original volume is 28 cu. ft. Find the external work, change of energy, and heat abstracted.

Ans. 21,240 ft.-lb.; 53,100 ft.-lb.; 95.6 B. t. u.

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19. During adiabatic expansion the temperature of air falls from 180° to −25° F. Find the ratios $p_2:p_1$ and $v_2:v_1$. Find the work done per pound of air. Ans. Work = 27,580 ft.-lb.

20. Air initially at atmospheric pressure and at a temperature of 70° F. is compressed according to the law $pv^{1.32}$ = const. to a pressure of 72 lb. per sq. in. and is then cooled at this pressure to the initial temperature. Find the total heat removed per pound of air. Ans. 70.9 B. t. u.

21. Taking an initial volume of 100 cu. ft. find the volume (*a*) at the end of compression (Ex. 20); (*b*) after cooling at constant pressure.

Ans. 30.01 cu. ft.; 20.42 cu. ft.

22. Take 1 lb. of air at a pressure of 20 lb. per sq. in. and temperature of 60° F. Find the volume and also the increase of volume when the temperature is raised one degree with the pressure remaining constant. Then show that the external work is $53.34(= B)$ ft.-lb. Assume some other initial state and show that the result is the same.

23. Combine the characteristic equation $pv = BT$ with the energy equation $dq = c_v dT + Apdv$ and deduce the equation

$$dq = c_p dT - Avdp.$$

Apply this equation to the process of heating a gas at constant pressure.

24. A non-conducting vessel is separated by a partition into two compartments. One compartment contains 5 cu. ft. of a gas at a pressure of 60 lb. per sq. in. and a temperature of 100° F.; the other contains 15 cu. ft. of the gas at a pressure of 20 lb. per sq. in. and a temperature of 40° F. The partition is removed and the gases mix. Find the pressure and temperature of the entire mass after mixing.

Ans. 30 lb. per sq. in.; 67.9° F.

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CHAPTER IV

THE SECOND LAW OF THERMODYNAMICS

40. Significance of the Second Law.—While the first law of thermodynamics gives a relation that must be satisfied during any change of state of a system, and of itself leads to many useful results, it is not sufficient to set at rest all questions that may arise in connection with energy transformations. It gives no indications of the *direction* of a physical process; it imposes no conditions upon the transformations of energy from one form to another except that there shall be no loss, and thus gives no indication of the possibilities of complete transformation of different forms; it furnishes no clue to the availability of energy for transformation under given circumstances. To settle these questions a second principle is required. This principle, called the **second law of thermodynamics,** has been stated in many ways. In effect, however, it is the principle of degradation of energy, just as the first law is the principle of the conservation of energy.

There are conceivable processes which, while satisfying the requirements of the first law, are declared to be impossible because of the restrictions of the second law. As a single example, it is conceivable that an engine might be devised that would deliver work without the expenditure of fuel, merely by using the heat stored in the atmosphere; in fact, such a device has been several times proposed. The first law would not be violated by such a process, for there would be transformation, not creation of energy; in other words, such an engine would not be a perpetual motion of the first class. Experience shows, however, that a process of this character, while not violating the conservation law, is nevertheless impossible. The statement of its impossibility is, in fact, one form of statement of the second law.

41. Availability of Energy.—In Art. 12 was noted the distinction between various forms of energy with respect to the pos-

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sibility of complete conversion. We shall now consider this matter somewhat in detail.

Mechanical and electrical energy stand on the same footing as regards possibility of conversion; either can be completely transformed into the other in theory, and nearly so in practice. Either mechanical or electrical energy can be completely transformed into heat. On the other hand, experience shows that heat energy is not capable of complete conversion into mechanical work, and to get even a part of heat energy transformed into mechanical energy, certain conditions must be satisfied. As a first condition, there must be two bodies of different temperature; it is impossible to derive work from the heat of a body unless there is available a second body of lower temperature. Suppose we have then a source S at temperature T_1 and a refrigerator R at lower temperature T_2; how is it possible to derive mechanical work from a quantity of heat energy Q_1 stored in S? If the bodies S and R are placed in contact, the heat Q_1 will simply flow from S to R and no work will be obtained. Hence, as a second condition, the systems S and R must be kept apart and a third system M must be used to convey energy. This third system is the **working fluid** or **medium.** In the steam plant, for example, the boiler furnace is the source S, the condenser is the refrigerator R at a lower temperature, and the steam is the medium or working fluid M. The medium M is placed in contact with S and receives from it heat Q_1; it then by an appropriate change of state (expansion) gives up energy in the form of work, and delivers to R a quantity of heat Q_2, smaller than Q_1, the difference $Q_1 - Q_2$ being the heat transformed into work. The details of this process will be described in following articles, where it will be shown that in no other way can a larger fraction of the heat be transformed into work.

The part of the heat Q_1 that can be thus transformed into work, that is, $Q_1 - Q_2$, is the **available** part of Q_1; and the part Q_2 that must be rejected to the refrigerator R, and which is of no further use, is the **unavailable** part of Q_1, or the **waste.** The ratio $\frac{Q_1 - Q_2}{Q_1}$ is called the **availability** of Q_1 for transformation into mechanical work. In general, the term availability signifies the fraction of the energy of a given system in a given state that can be transformed into mechanical work.

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42. Reversibility.—The processes described in thermodynamics are either reversible or irreversible. A process is said to be **reversible** when the following conditions are fulfilled:

(*a*) When the direction of the process is reversed, the system taking part in the process can assume in inverse order the states traversed in the direct process.

(*b*) The external actions are the same for the direct and reversed processes or differ by an infinitesimal amount only.

(*c*) Not only the system undergoing the change but all connected systems can be restored to initial conditions.

A process which fails to meet these requirements in any particular is an **irreversible** process.

There are three essentially irreversible processes that demand special consideration.

1. The direct conversion of work into heat through the agency of friction. Consider, for example, the heating of a journal and bearing or the heating of water by churning, as in Joule's experiment. It is manifestly impossible for the process to proceed in the reverse order, that is, for the shaft and bearing to cool and restore the work previously expended or for the water to cool and drive the paddle wheel backward. Furthermore, it is impossible with the aid of external agencies to cool the water to its original state and restore the work expended without leaving changes in external systems.

2. The conduction of heat from a body at temperature t_1 to another at temperature t_2 is an irreversible process. In order that heat shall flow in the direction indicated t_1 must be greater than t_2. The heat will not of itself flow back from the colder to the hotter body. By means of a refrigerating machine it can be taken from the colder body and transferred to the hotter body, but this process involves the expenditure of work, and consequently changes in external systems.

3. A third irreversible process of importance is the *throttling* or *wire-drawing* of a fluid in flowing through an orifice from a region of high pressure to a region of lower pressure. Examples are seen in the passage of steam through reducing valves, in the flow of liquid ammonia through the expansion valve of the refrigerating machine.

It is evident that the process cannot be directly reversed;

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that is, the fluid will not of itself flow back into the region of high pressure. By compression the fluid itself can be restored to its initial condition, but as a result one external system, the compressor, has given up work, a second external system has received heat, and by no possible means can the heat received by the second system be transformed back into the work lost by the first external system.

In the strict sense of the term, there are no reversible processes in nature, since no process is entirely free from friction or heat conduction. There are, however, two important processes that may be made to approach reversibility as a limiting condition.

1. The compression or expansion of a gas. Suppose the gas to be confined in a cylinder with a movable piston and let p be the internal pressure of the gas. Then by making the external pressure on the piston $p + \delta p$ the gas will be compressed, while if it is made $p - \delta p$ the gas will expand. The process is reversed by a change in the external pressure which may be made as small as we please; hence it approaches the limiting condition of reversibility.

2. Transfer of heat between bodies of the same temperature. Let the body A have the temperature t and a second body B the temperature $t - \delta t$; in this case heat will flow from A to B. By changing the sign of δt the direction of the flow is reversed. As δt is made to approach zero, the infinitely slow process of heat conduction may be regarded as reversible. In this case the reversal is accomplished by an infinitesimal change in the temperature.

43. Statements of the Second Law.—According to the first law, the total quantity of energy in a system of bodies cannot be increased or decreased by any change, reversible or irreversible, that may occur within the system. It is not, however, the *total* energy, but the *available* energy of the system that is of importance; and experience shows that a change within the system usually results in a change in the availability of the energy of the system.

It may be considered as almost self-evident that no change of a system which will take place of itself can increase the available energy of the system; on the other hand, experience teaches that all actual changes involve loss of availability. Consider,

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for example, the flow of heat from a body of temperature t_1, to another at temperature t_2. For the flow to occur of itself we must have $t_1 > t_2$, and as a result of the process there is a loss of availability. To produce an increase of availability would require t_2 to be greater than t_1; in that case, however, the process would not be possible. In the limiting reversible case, $t_2 = t_1$, the availability remains unchanged. A consideration of other physical processes within the range of experience leads to similar results. We may, therefore, lay down the following general laws, which, like the law of conservation of energy, are based on experience:

I. *No change in a system of bodies that can take place of itself can increase the available energy of the system.*

II. *An irreversible change causes a loss of availability.*

III. *A reversible change does not affect the availability.*

These statements may be regarded as fundamental laws underlying all physical and chemical changes. The second and third together constitute the law of degradation of energy. The first may be taken as a general statement of the second law of thermodynamics.

By considering special processes the general statement of the second law here given may be thrown into special forms. Thus if heat could of itself pass from a body of lower to a body of higher temperature, the result of the process would be an increase of available energy, a result that is impossible according to our first statement. We have, therefore, Clausius' form of the second law, viz.:

It is impossible for a self-acting machine unaided by any external agency to convey heat from one body to another at higher temperature.

Again, if we consider the increase of available energy that would result from deriving work directly from the heat of the atmosphere, we are led to Kelvin's statement, namely:

It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of surrounding objects.

44. Carnot's Cycle.—In order to estimate the available energy of a system in a given state, or the loss of available energy when the system undergoes an irreversible change, it is

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necessary to know the most efficient means of transforming heat into mechanical work under given conditions. This knowledge is furnished by a study of the ideal processes first described by Carnot in 1824.

Suppose that the conditions stated in Art. 41 are furnished; that is, let there be a source of heat S at temperature T_1, a refrigerator R at a lower temperature T_2, and an intermediate system, the working fluid or medium M. The medium we may assume to be inclosed in a cylinder provided with a piston (Fig. 10).

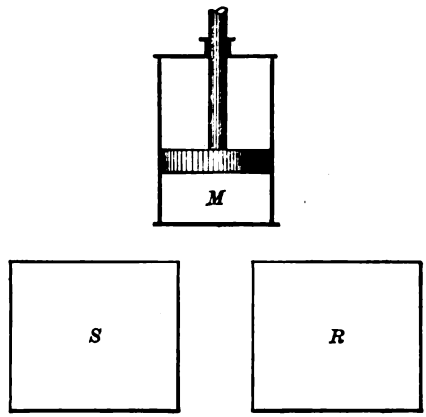


FIG. 10.

Let the medium initially in a state represented by B (Fig. 11), at the temperature T_1 of the reservoir S, expand adiabatically until its temperature falls to T_2, the temperature of body R. By this expansion the state C is reached, and the work done by the medium is represented by the area B_1BCC_1.

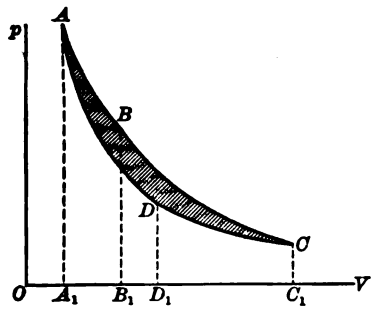


FIG. 11.

The expansion is assumed to proceed slowly so that the pressures on the two faces of the piston are sensibly equal, and the process is, therefore, reversible. The cylinder is now placed in contact with R so that heat can flow from M to R, and the medium is compressed. The work represented by the area C_1CDD_1 is done on the medium, and heat Q_2 passes from the medium to the refrigerator. The process is again assumed to be so slow as to be reversible. From the state D the medium is now compressed adiabatically, the cylinder being removed from R, until its temperature again becomes T_1, that of the source S. During this third process work represented by the area D_1DAA_1

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is done on fluid. Finally, the cylinder is placed in contact with S and the fluid is allowed to expand at the constant temperature t_1 to the inital state B. Work represented by the area A_1ABB_1 is done by the fluid during this process, and the temperature is kept constant by the flow of heat Q_1 from S to M.

The area $ABCD$ inclosed by the four curves of the cycle represents the mechanical work gained; that is, the excess of work done by the medium over that done on the medium. Denoting this by W, we have from the first law,

$$Q_1 - Q_2 = AW. \tag{1}$$

The efficiency of the cycle is the ratio of the work gained to the heat supplied from the source S. Denoting the efficiency by η, we have

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{AW}{Q_1}. \tag{2}$$

Since all the processes of the Carnot cycle are reversible, it is evident that they may be traversed in reverse order. Thus starting from B, the fluid is compressed isothermally from B to A and gives up heat Q_1 to S; from A to D it expands adiabatically, from D to C it expands at the constant temperature T_2 and in so doing receives heat Q_2 from R; finally it is compressed adiabatically from C to the initial state B. In this case the work W represented by area $ABCD$ is done *on* the fluid M, heat Q_2 is taken from the refrigerator R, and the sum $Q_2 + AW = Q_1$ is delivered to the source S. This ideal reversed engine is the basis of modern refrigerating machines.

45. Carnot's Principle.—The efficiency of Carnot's ideal engine evidently depends upon the temperatures T_1 and T_2 of the source and refrigerator, respectively. The question at once arises whether the efficiency depends also upon the properties of the substance M used as a working fluid. The answer is contained in Carnot's principle, namely:

Of all engines working between the same source and the same refrigerator, no engine can have an efficiency greater than that of a reversible engine.

In other words, all reversible engines working between the same temperature limits T_1 and T_2 have the same efficiency; that is, *the efficiency is independent of the working fluid.*

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The proof of Carnot's principle rests on the second law, and consists essentially in showing that if any engine A is more efficient than a reversible engine B working between the same temperatures, then A and B can be coupled together in such a way as to produce available energy without a compensating loss of availability.

Suppose the two engines A and B (Fig. 12) to take equal quantities of heat Q_1 from the source when running direct. Then, since by hypothesis A is the more efficient,

$$W_A > W_B$$

and

$$Q_2^A < Q_2^B.$$

Now let engine B be run reversed. It will take heat Q_2^B from R and deliver Q_1 to S. If A and B are coupled together, A will run B reversed and deliver in addition the work $W_A - W_B$. The source is unaffected since it simultaneously receives heat Q_1 and gives up heat Q_1. The refrigerator, however, loses the heat $Q_2^B - Q_2^A$, which is the equivalent of the work $W_A - W_B$ gained. We have, therefore, an arrangement by which unavailable energy in the form of heat in the reservoir is transformed into mechanical work. In other words, by a self-acting process the available energy of the system of bodies S, R, A, and B is increased. According to the second law (Art. 43), such a result is impossible; if such a result were possible, power in any quantity could be obtained from the heat stored in the atmosphere without consumption of fuel.

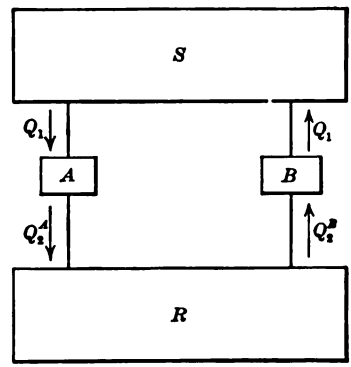


FIG. 12.

The assumption that engine A is more efficient than the reversible engine B leads to a result that experience has shown to be impossible. We conclude, therefore, that the assumption is not admissible and that engine A cannot be more efficient than engine B. But if engine A is also reversible, B cannot

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be more efficient than A, and it follows that all reversible engines between the same source and the same refrigerator are equally efficient.

Since the efficiency of the reversible Carnot engine is independent of the properties of the medium and depends upon the temperatures of source and refrigerator only, we have

$$\eta = \frac{AW}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = f(t_1,t_2), \tag{1}$$

whence
$$\frac{Q_2}{Q_1} = 1 - \eta = F(t_1,t_2); \tag{2}$$

that is, the quotient $\frac{Q_2}{Q_1}$ is some function of the temperatures t_1 and t_2. The form of this function is required.

46. Thermodynamic Scale of Temperature.—In the operation of the Carnot engine we observe that the heat Q_1 absorbed from the source at the higher temperature t_1 is greater than the heat Q_2 rejected to the refrigerator at lower temperature t_2; that is,

$$Q_1 > Q_2 \text{ when } t_1 > t_2.$$

Let θ_1 and θ_2 be two numbers proportional, respectively, to Q_1 and Q_2,

whence
$$\frac{\theta_2}{\theta_1} = \frac{Q_2}{Q_1}, \text{ and } \theta_1 > \theta_2.$$

If the refrigerator at temperature t_2 is taken as a source and a third body at a still lower temperature t_3 is used as a refrigerator, then if heat Q_2 is taken from the source a smaller quantity Q_3 will be delivered to the refrigerator. Again let θ_3 be a number that has the same ratio to Q_3 that θ_2 has to Q_2. Proceeding in this way we get a series of numbers θ_1, θ_2, θ_3, θ_4, etc. associated with the successive bodies used as source and refrigerators. In order of magnitude the numbers follow the temperatures of the bodies; thus the largest number is associated with the body of highest temperature.

The numbers θ_1, θ_2, θ_3, . . . may be taken to establish a scale of temperatures. If this scale is adopted, we have for the efficiency of the Carnot engine

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{\theta_2}{\theta_1}. \tag{1}$$

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The scale of temperatures arrived at from the investigation of Carnot's cycle was first proposed by Lord Kelvin in 1848, and is known as the **absolute scale** because it is independent of the property of any substance. The scale is simply such that any two temperatures on it are proportional to the quantities of heat absorbed and rejected by a reversible Carnot engine working between these temperatures.

If in (1) we make $Q_2 = 0$, $\eta = 1$ and $\theta_2 = 0$. If we conceive a temperature lower than the zero on the absolute scale, that is, if we assume a negative value for θ_2, then $\frac{\theta_1 - \theta_2}{\theta_1} > 1$, and the engine has an efficiency greater than 1, or transforms more heat into work than it receives from the source. Such an assumption is clearly inadmissible, and it follows that the zero of Kelvin's absolute scale is an absolute zero, and the temperature corresponding to it is the lowest temperature conceivable. We are thus led to the conception of an absolute zero independent of the properties of any particular substance.

47. Carnot's Cycle for a Perfect Gas.—The efficiency of the Carnot cycle in terms of the temperatures of the source and refrigerator on the perfect gas scale may be deduced from the laws of gases given in Chap. III. Referring to Fig. 11, let T_1 denote the constant absolute temperature (on the gas scale) along the isothermal AB, and T_2 the constant temperature along the isothermal CD; also let the subscripts a, b, c, d indicate pressures and volumes at the points A, B, C, D. For the adiabatic change BC, we have

$$\frac{T_b}{T_c} = \frac{T_1}{T_2} = \left(\frac{V_c}{V_b}\right)^{k-1}; \tag{1}$$

likewise for the adiabatic AD

$$\frac{T_a}{T_d} = \frac{T_1}{T_2} = \left(\frac{V_d}{V_a}\right)^{k-1}. \tag{2}$$

Therefore

$$\frac{V_c}{V_b} = \frac{V_d}{V_a}, \quad \text{or} \quad \frac{V_c}{V_d} = \frac{V_b}{V_a}. \tag{3}$$

The heat absorbed by the medium during the isothermal expansion AB is (See Art 35).

$$Q_1 = ABT_1 \log_e \frac{V_b}{V_a} \tag{4}$$

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and the heat rejected during the isothermal compression CD is

$$Q_2 = ABT_2 \log_e \frac{V_c}{V_d} = ABT_2 \log_e \frac{V_b}{V_a}. \tag{5}$$

The efficiency is therefore

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2 \cdot AB \log_e \frac{V_b}{V_a}}{T_1 \cdot AB \log_e \frac{V_b}{V_a}} = 1 - \frac{T_2}{T_1}. \tag{6}$$

The expression of the efficiency given by (6) for a perfect gas must be identical with the expression given by (1), Art. 46, which applies to all media. Hence we have

$$1 - \frac{T_2}{T_1} = 1 - \frac{\theta_2}{\theta_1}, \qquad \text{or} \qquad \frac{T_2}{T_1} = \frac{\theta_2}{\theta_1}. \tag{7}$$

When $T_2 = 0$, $\theta_2 = 0$; therefore the zero of Kelvin's thermodynamic scale coincides with the zero of the gas scale; and by a proper choice of the value of θ at some well-known temperature, as the melting point of ice, the thermodynamic scale throughout may be made identical with the perfect-gas scale.

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CHAPTER V

AVAILABLE ENERGY AND ENTROPY

48. Efficiency of the Carnot Engine as a Measure of Availability.—Under certain conditions, the efficiency of the ideal Carnot engine furnishes a means of measuring the available part of the energy in a system, and the loss of available energy incurred in an irreversible change of state.

We consider first the heat energy stored in a system having the absolute temperature T in the presence of a refrigerator at temperature T_0. It is assumed that the source is so large that its temperature is not sensibly reduced by the withdrawal of a finite quantity of heat Q, and likewise that the refrigerator (say the atmosphere) may absorb a finite quantity of heat Q_0 without rise of temperature.

Let the quantity of heat Q be taken from the source and furnished to a Carnot engine operating between the temperature limits T and T_0. Then the part of Q that may be transformed into work, or the available part is

$$Q_a = Q\left(1 - \frac{T_0}{T}\right), \tag{1}$$

and the waste, or unavailable part is

$$Q_b = Q - Q_a = Q\frac{T_0}{T}. \tag{2}$$

It should be noted that Q_a is the absolute maximum available energy under the conditions and that Q_b is the minimum waste. Any departure from ideal conditions results in a decrease of Q_a and a corresponding increase of Q_b.

The temperature T_0 cannot be lower than that of surrounding objects, *i.e.* the atmosphere[1]; for even if a refrigerator could

[1] Under special conditions a refrigerator whose temperature is permanently below that of the atmosphere may exist; *e.g.* the water of the ocean or of one of the great lakes.

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be found with a temperature lower than that of the atmosphere, it could not be maintained in that state. Hence, the temperature of the atmosphere imposes a natural limitation on the availability of heat in the performance of work.

EXAMPLE. If the absolute temperature of a source is 1000° F. and that of the atmosphere is 520°, the available energy is

$$\frac{1000 - 520}{1000} = 0.48 \text{ of the total energy.}$$

Therefore, for every 1000 B. t. u. received from the source, not more than 480 B. t. u. can by any means whatever be transformed into work, and at least 520 B. t. u. must be rendered unavailable.

49. Finite Source.—In case the source is a finite system so that the abstraction of heat from it lowers the temperature, the varying temperature of the source must be taken into account in estimating the available energy. The following example illustrates this case.

EXAMPLE. Let heat be applied to a vessel containing 40 lb. of water initially at 60° F. and suppose the final temperature to be 190° F. With a refrigerator at $T_0 = 500$, the total energy received by the water and the available part of that energy are required.

Taking the specific heat of water as 1, the energy absorbed by the water is

$$40 \times 1 \times (190 - 60) = 5200 \text{ B. t. u.}$$

Having the water at the upper temperature, 190° ($T = 649.6$), assume that the water is used as a source for a Carnot engine with the refrigerator at $T_0 = 500$.

Let 40 B. t. u. be removed from the water; the temperature drops one degree and the mean absolute temperature of the source during this process is 649.1. The removal of the second 40 B. t. u. reduces the temperature one degree and the mean temperature is 648.1, and so on. Hence, we have for the successive steps

1. $\Delta Q'_a = 40\left(1 - \frac{500}{649.1}\right)$, $\qquad \Delta Q'_b = 40\,\frac{500}{649.1}$.

2. $\Delta Q''_a = 40\left(1 - \frac{500}{648.1}\right)$, $\qquad \Delta Q''_b = 40\,\frac{500}{648.1}$.

There will be 130 of these steps. In the last one the temperature is reduced from 61° to 60° F., the mean absolute temperature is 520.1 and for this process therefore

$$\Delta Q_a = 40\left(1 - \frac{500}{520.1}\right). \qquad \Delta Q_b = 40\,\frac{500}{520.1}.$$

The total available energy is obtained by adding the 130 elements ΔQ_a.

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Evidently the integration process may be used advantageously. If heat ΔQ is taken from the water when its temperature is T, then

$$\Delta Q = 40\,\Delta T,$$

$$\Delta Q_a = 40\,\Delta T\left(1 - \frac{T_0}{T}\right). \qquad \Delta Q_b = 40\,\Delta T\,\frac{T_0}{T}.$$

For the total unavailable energy we have therefore

$$Q_b = \Sigma\Delta Q_b = \sum_{T_1}^{T_2} 40\,\Delta T\,\frac{T_0}{T} = 40\,T_0\sum_{T_1}^{T_2}\frac{\Delta T}{T};$$

or passing to the definite integral

$$Q_b = 40\,T_0\int_{T_1}^{T_2}\frac{dT}{T} = 40\times 500\int_{519.6}^{649.6}\frac{dT}{T}$$
$$= 40\times 500\times \log_e\frac{649.6}{519.6} = 4466 \text{ B. t. u.}$$

Hence $Q_a = Q - Q_b = 5200 - 4466 = 734$ B. t. u.

If the same quantity of heat, 5200 B. t. u. were taken from an infinite source, the temperature therefore remaining at 190°, the available energy would be

$$Q_a = 5200\left(1 - \frac{500}{649.6}\right) = 1197 \text{ B. t. u.}$$

50. Energy Changes in Heating or Cooling.—Let a system of weight M and having the specific heat c have its temperature increased from T_1 to T_2 by the absorption of heat from external sources; and let T_0 denote the lowest available temperature.

The heat energy absorbed by the system is

$$Q = Mc(T_2 - T_1). \tag{1}$$

Of the energy thus received, part is available part is unavailable; that is, the available energy of the system is increased as is also the unavailable energy. The increase of the system's unavailable energy according to the discussion just preceding is

$$Q_b = T_0\int_1^2\frac{dQ}{T}, \tag{2}$$

or since $dQ = McdT$,

$$Q_b = McT_0\int_{T_1}^{T_2}\frac{dT}{T} = McT_0\log_e\frac{T_2}{T_1}, \tag{3}$$

assuming c to be constant. The increase of available energy is

$$Q_a = Q - Q_b. \tag{4}$$

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In case the system gives out heat, as by radiation, dQ has the negative sign and Q_b is therefore negative, indicating a loss of unavailable energy.

In the case of melting or vaporization the heat received by the system is used to change the state of aggregation and the temperature remains constant. Equation (2) is still applicable, but since T is constant it takes the simple form

$$Q_b = \frac{T_0}{T}\int_1^2 dQ = \frac{T_0}{T}Q.$$

EXAMPLE. The heat required to change one pound of water to steam at a constant temperature of 212° is found to be 971.7 B. t. u. If T_0 is 550°, the unavailable part of the heat supplied is

$$\frac{550}{212 + 459.6} \times 971.7 = 833.3 \text{ B. t. u.},$$

and the available part is

$$971.7 - 833.3 = 138.4 \text{ B. t. u.}$$

51. Irreversible Conversion of Work into Heat.—In all processes that involve friction the work done against the forces of friction is converted into heat. For heat thus produced we shall use the symbol H, reserving Q to denote heat brought into the system from outside. As a simple example of such a process, suppose a mass of water to be churned by a paddle, the work required to drive the paddle being furnished by a motor or other external means. The temperature of the water is raised from T_1 to T_2, the heat required is

$$H = Mc(T_2 - T_1)\text{B.t.u.} \tag{1}$$

and the motor therefore furnishes the work JH ft. lb. Following the same line of reasoning as in the preceding article, the unavailable energy of the water is increased by

$$H_b = T_0\int_1^2 \frac{dH}{T} = McT_0\int_{T_1}^{T_2}\frac{dT}{T} = McT_0 \log_e \frac{T_2}{T_1}, \tag{2}$$

and the available energy is increased by the amount

$$H_a = H - H_b. \tag{3}$$

Observe that the motor gives up available energy H while the

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water receives the available energy H_a; consequently there is on whole, a loss of available energy

$$H - H_a = H_b. \tag{4}$$

In many instances the work is not furnished from external sources and the process is wholly internal. For example, in the flow of steam through a turbine, there is friction between the moving steam and the nozzles and blades and fluid frictional losses due to internal whirls and eddies. As a result some of the kinetic energy of the moving current of steam is converted into heat. Wiredrawing of fluids through parts or valves is always accompanied by the generation of heat through friction. In all such cases there is an increase of the unavailable energy of the system given by the expression

$$H_b = T_0 \int \frac{dH}{T}.$$

Since, however, no energy is supplied from external sources, this gain of unavailable energy must represent a corresponding loss of available energy.

52. Conduction of Heat.—If several parts of a system have different temperatures T_1, T_2, etc., flow of heat from one part to another with the resulting equalization of temperature will affect the available energy of the system. This fact may be shown by a numerical example.

EXAMPLE. Let 40 lb. of water at 50° F. be mixed with 60 lb. at 200° F. Required the change of available energy, taking $T_0 = 500$.

The temperature after mixing is 140° F.; hence we have to compare the available energy of 100 lb. at 140° F. with the sum of the available energies of 40 lb. at 50° F. and 60 lb. at 200° F. The three absolute temperatures involved are 509.6, 659.6, and 599.6.

The unavailable energy in the 40 lb. at 50° is

$$McT_0 \int_{T_0}^{T_1} \frac{dT}{T} = 40 \times 500 \log_e \frac{509.6}{500} = 380.4 \text{ B. t. u.}$$

That of the 60 lb. at 200° is $60 \times 500 \log_e \frac{659.6}{500} = 8310.6$ B. t. u.

That of 100 lb. at 130° is $100 \times 500 \log_e \frac{599.6}{500} = 9082.5$ B. t. u.

Increase of unavailable energy = 9082.5 − (8310.6 + 380.4) = 391.5 B. t. u. Since the unavailable energy is increased by 391.5 B. t. u. the available energy is decreased by the same amount.

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Let $M_1, M_2, M_3, \ldots$ denote the weights of the different parts of the system, $T_1, T_2, T_3, \ldots$ the corresponding absolute temperatures, c_1, c_2, c_3 the specific heats, T' the common temperature after thermal equilibrium, and T_0 the lowest available temperature. Then the increase of unvailable energy due to heat conduction between the parts is

$$\Delta U_b = T_0(M_1c_1 + M_2c_2 + \ldots) \log_e \frac{T'}{T_0} -$$

$$[T_0M_1c_1 \log_e \frac{T_1}{T_0} + T_0M_2c_2 \log_e \frac{T_2}{T_0} + \ldots],$$

or

$$\Delta U_b = T_0\Sigma,$$

where Σ denotes the algebraic sum of the terms of the form $Mc \log_e \frac{T}{T_0}$ and is always positive in sign.

53. Unavailable Energy of a System.—The energy U_1 of a system in the initial state 1 is made up of two part, the available energy U_{1a} and the unavailable part U_{1b}. If the system passes through a series of processes but ultimately returns to its initial state 1 the energy attains its initial value U_1, and evidently the available and unavailable parts U_{1a} and U_{1b} likewise are the same as at the beginning, provided the refrigerator temperature T_0 has not changed meanwhile. Therefore the change of unavailable energy, like the change of total energy, between two states is independent of the path, and such change may be written as the difference $U_{2b} - U_{1b}$.

We now investigate the means by which the unavailable energy of a non-isolated system may be changed.

1. Let the system absorb heat from external bodies. The increase of unavailable energy from this source is

$$T_0 \int_1^2 \frac{dQ}{T}.$$

The sign of this term may be either positive or negative, the negative sign indicating rejection of heat and therefore loss of unavailable energy. It should be noted that in this process other systems are affected and that they experience changes of energy along with the system under consideration.

2. If there is conversion of work into heat because of internal

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friction the unavailable energy of the system is increased by the amount

$$T_0 \int_1^2 \frac{dH}{T}.$$

The work *may* be furnished by an external system; but in most cases it is an internal occurrence, and the system under consideration is the only one affected. The increase of unavailable energy means an equal decrease of available energy. The sign of this term can only be positive.

3. If heat flows from one part of the system to another on account of differences of temperature, the unavailable energy is increased by the amount

$$T_0 \Sigma,$$

in which Σ is necessarily a positive quantity. This process is internal, and the unavailable energy increases at the expense of the available energy.

4. Let the system be slowly compressed thus receiving mechanical energy from an outside system. Since the process is reversible all this energy is available; therefore the change of unavailable energy is zero.

Summing up these changes for the processes to which the system is ordinarily subjected, we have for the total change of unavailable energy

$$U_{2b} - U_{1b} = T_0 \int_1^2 \frac{dQ}{T} + T_0 \int_1^2 \frac{dH}{T} + T_0 \Sigma.$$

54. Entropy.—It will be observed that each of the terms in the preceding expression for the increase of unavailable energy contains T_0. Hence we see that the unavailable energy depends directly on the refrigerator temperature; the lower that temperature the smaller the unavailable energy.

Let the ratio $U_b : T_0$ be denoted by the symbol S; then the preceding equation may be given the form

$$\frac{U_{2b}}{T_0} - \frac{U_{1b}}{T_0} = S_2 - S_1 = \int_1^2 \frac{dQ}{T} + \int_1^2 \frac{dH}{T} + \Sigma. \qquad (1)$$

The ratio S is called the **entropy** of the system, and therefore $S_2 - S_1$ is the change of entropy of the system between the states 1 and 2.

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As thus defined, entropy is simply proportional to unavailable energy. It is assumed that the energy U of the system relative to some standard state is known, and that the unavailable part U_b can be determined; then the entropy S is simply U_b divided by the refrigerator temperature T_0. Evidently S, like U_b, depends upon the state of the system only. The change of U_b between states 1 and 2, however, depends upon T_0, while the change of S between the two states is fixed and definite.

If the internal irreversible processes due to friction and heat conduction are absent, then $H = 0$, $\Sigma = 0$, and equation (1) becomes simply

$$S_2 - S_1 = \int_1^2 \frac{dQ}{T}. \tag{2}$$

This equation is sometimes used as the definition of entropy, but it is applicable to reversible frictionless processes only.

55. Entropy and Energy Changes in an Isolated System. According to the conservation law, the energy U of an isolated system remains constant; however, as the result of processes within the system, the available part of U may suffer a change. Two cases have already been noted. (1) The conversion of work into heat in the interior of an isolated system results in a change of available into unavailable energy of amount $T_0 \int \frac{dH}{T}$. (2) Conduction of heat between the parts of an isolated system increases the unavailable energy by $T_0\Sigma$ at the expense of the available energy.

Consider now the case of heating a system from an external source. Let X denote the system receiving heat and Y the source of heat; then X and Y together may be regarded as a single isolated system made up of two parts. Suppose that system Y is a large source at temperature T' and that heat Q is transmitted to system X thereby raising its temperature from T_1 to T_2. Assuming that T' remains constant the source Y gives up the energy Q of which

$$Q\frac{T_0}{T'} = T_0\frac{Q}{T'}$$

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is unavailable. The system X receives energy Q and in this system the part

$$T_0 \int_1^2 \frac{dQ}{T}$$

is unavailable. Since T' is greater than T_1 and T_2, it is evident that $\frac{Q}{T'} < \int_1^2 \frac{dQ}{T}$; hence, on the whole, there is a gain of unavailable energy

$$\Delta U_b = T_0 \int_1^2 \frac{dQ}{T} - T_0 \frac{Q}{T'}$$

The total energy is unchanged since Y gives up heat Q which is received by X; therefore the available energy is decreased. An example will illustrate this point.

In the example of Art. 49, the heat absorbed by 40 lb. of water in raising the temperature from 60° to 190° F. was 5200 B. t. u. of which 734 B. t. u. was found to be available and 4466 B. t. u. unavailable. Assume that the heat was absorbed from a large body of hot gas having an absolute temperature of 2000°. With $T_2 = 500°$, the unavailable part of 5200 B. t. u. in the system of hot gas is $5200 \times \frac{500}{2000} = 1300$ B. t. u. The changes of energy in the two systems may be exhibited as follows:

	Δu	Δu_b	Δu_a
Water (system X).....	+5200	+4466	+ 734
Hot gas (system Y).....	−5200	−1300	−3900
Isolated system (X and Y).....	0	+3166	−3166

The effect of the process is a change of about 60 per cent of the energy transferred from the available to the unavailable condition.

The only processes that can take place in an isolated system without an increase of unavailable energy are the strictly reversible processed. Such processes are never realized. Transfer of heat from one body, to another within the system requires a finite temperature difference; it is therefore irreversible and involves a loss of available energy. If work is done by one part of the system on another some of the work must be degraded into heat because of unavoidable friction.

We conclude, therefore, that all occurrences within an isolated system involve degradation of energy, that is, an increase of unavailable energy at the expense of available energy.

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If the increase of unavailable energy ΔU_b is divided by T_0 the quotient is the increase of entropy ΔS. Hence we may say that all processes that occur in an isolated system result in an increase of the entropy of the system; and that the increase of entropy *of an isolated system* measures the degradation of energy involved.

56. Characteristics of Entropy.—From the definition of entropy, namely, the ratio of the unavailable energy of a system to the lowest available temperature, certain important conclusions follow immediately.

1. The entropy of a system, like the volume and energy, depends upon the mass of the system. That is, the entropy of M lb. of a substance is M times the entropy of 1 lb. As usual, s denotes the entropy of unit weight, S the entropy of weight M; then $S = Ms$.

2. Entropy like energy is additive. If a system consists of several bodies having entropies S_1, S_2, S_3, etc., the entropy of the system is

$$S = S_1 + S_2 + S_3 + \ldots .$$

However, if two gases having initially entropies S_1 and S_2 are mixed, the entropy of the mixture will exceed the sum $S_1 + S_2$ if the mixing process is irreversible.

3. Entropy, like energy, is relative, and any expression for the entropy of a system contains an unknown constant of integration. Since we are concerned only with differences of entropy, this constant disappears on subtraction and therefore introduces no difficulty. In assigning numerical values to the entropy of a system it is customary to assume the entropy as zero at some standard state. Thus in the tables of the properties of steam and ammonia, the entropy of the liquid at 32° F. is taken as zero.

4. If energy is measured in thermal units, the unit of entropy is B. t. u. per degree F. This unit has no name.

5. The entropy of a system is the same whenever the system is in the same physical state. If the system, starting from some initial state, undergoes a series of reversible or irreversible processes but is ultimately brought back to the initial state, the entropy will have its initial value. In other words, the entropy of a system is a function of the state only.

6. The entropy being a function of the coördinates of the

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system may itself be used as a coördinate to define the state of the system.

7. For a strictly reversible process, the change of entropy is given by the integral $\int \frac{dQ}{T}$. Hence the change of entropy between states A and B may be found by choosing *any* reversible path between A and B and evaluating the integral $\int_A^B \frac{dQ}{T}$ for this path.

57. Entropy as a Coördinate.—The fact that the entropy of a system is a function of the state only permits the use of entropy as one of the coördinates defining the state of the system. At present, therefore, we have five coördinates, p, v, t, u, and s, that may be used. From these five, ten pairs may be selected and the change of state of a system may be represented by ten different curves on ten different planes.

As we have seen, graphical representation on the pV-plane (the indicator diagram) is of special importance because the area between the curve and the V-axis represents the external work. Of equal interest is graphical representation on a plane having the absolute temperature T as the ordinate and the entropy S as the abscissa; for with proper restrictions, the area between the curve and the S axis represents the heat absorbed by the system from external sources.

The choice of the temperature T as one of the coördinates involves the assumption that the system under consideration has the same temperature throughout all its parts; hence there can be no increase of entropy due to conduction of heat within the system. With this assumption the equation for the increase of entropy of the system (Art. 54) becomes

$$S_2 - S_1 = \int_1^2 \frac{dQ}{T} + \int^2 \frac{dH}{T}, \tag{1}$$

or written in the differential form

$$dS = \frac{dQ}{T} + \frac{dH}{T}. \tag{2}$$

From this form we obtain

$$TdS = dQ + dH, \tag{3}$$

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whence $$\int_1^2 TdS = \int_1^2 dQ + \int_1^2 dH = {}_1Q_2 + {}_1H_2. \quad (4)$$

Let a change of state be represented in TS-coördinates by the path AB, Fig. 13, A and B denoting, respectively, the initial and final states. Consider an element between the curve AB and the S-axis. Its width is ΔS and its altitude is T, hence its area is $T\Delta S$. Evidently the area A_1ABB_1 is the limit of the sum of these elements, that is, it represents the definite integral $\int_A^B TdS$. But from (4) this integral is ${}_aQ_b + {}_aH_b$, that is, the sum of the heat absorbed from outside and the heat generated inside the system through friction.

If the process is frictionless, $H = 0$, and the *area between the curve and the S-axis represents the heat absorbed by the system.* If, on the other hand, the process is adiabatic but not frictionless, then $Q = 0$, and the area represents the heat generated within the system.

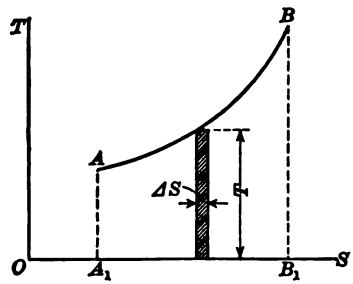


FIG. 13.

58. Absorption of Heat.—Let us consider the process of heating a system from external sources, as, for example, the heating of water in a boiler. The process is assumed to be frictionless. Referring to Fig. 13, the ordinate A_1A represents the initial absolute temperature of the system. If now we suppose this ordinate moved to the right and at the same time stretched in such a way that the length of the ordinate always represents the absolute temperature of the system while the area swept over from the initial position A_1A represents the heat absorbed, then the upper end of the ordinate will describe a curve, as AB, representing the change of state of the system.

The general course of this curve may be predicted from the following considerations:

1. If the temperature is increasing the state point must move upward, that is, away from the S-axis.

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2. If the temperature is decreasing the state point must move toward the S-axis.

3. If the system is absorbing heat the entropy must be increasing, that is, the state point must be moving to the right, or away from the T-axis.

4. If the system is rejecting heat the state point must be moving to the left, or toward the T-axis.

The equation of the TS-curve representing the absorption of heat may be obtained as follows. If c is the specific heat of the system, we have the general equation

$$dQ = McdT, \tag{1}$$

whence

$$dS = \frac{dQ}{T} = Mc\frac{dT}{T}. \tag{2}$$

If the specific heat is constant, the integration of (2) gives the equation

$$S - S_1 = Mc\int_{T_1}^{T}\frac{dT}{T} = Mc\log_e\frac{T}{T_1}. \tag{3}$$

If the specific heat is variable, it can usually be expressed as a function of the temperature; that is, we can write

$$c = f(T),$$

whence

$$s - s_1 = \int_{T_1}^{T}\frac{f(T)dT}{T}. \tag{4}$$

The integration can be effected when the function $f(T)$ is known.

EXAMPLE. Let the specific heat of a substance be given by the relation

$$c = a + bt = a + b(T - 459.6);$$

we have then

$$s_2 - s_1 = (a - 459.6\,b)\int_{T_1}^{T_2}\frac{dT}{T} + b\int_{T_1}^{T_2}dT$$

$$= (a - 459.6\,b)\log_e\frac{T_2}{T_1} + b(T_2 - T_1).$$

The general form of the curve is shown in Fig. 14. It is a property of this curve that the subtangent of the curve is numerically equal to the specific heat. Thus from the figure we have

$$EF = EP\cot\phi$$

$$= T\frac{ds}{dT} = \frac{dq}{dT} = c.$$

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It follows that the smaller the value of c, the greater the slope of the curve.

Cases may arise in which the slope of the TS-curve is negative, as shown in Fig. 15. In such cases abstraction of heat is accompanied by a rise in temperature or *vice versa*. Evidently

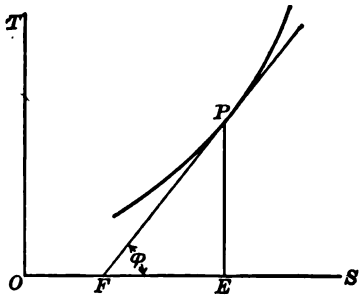


FIG. 14.

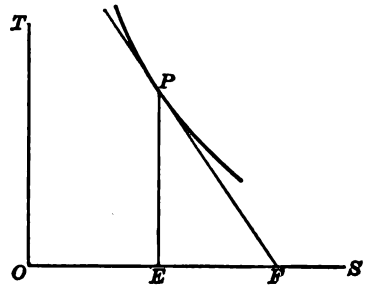


FIG. 15.

the specific heat $\frac{dq}{dT}$ must be negative, as is indicated geometrically by the negative subtangent. Examples will be shown in the compression of air in the ordinary air compressor, and in the expansion of dry saturated steam with the provision that it remains dry during the expansion.

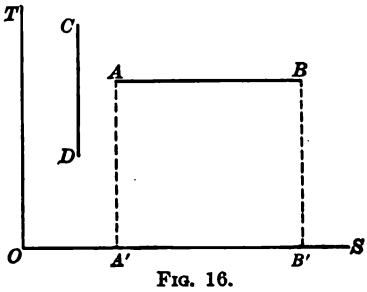


FIG. 16.

59. Isothermal Change of State.—If the temperature of the system remains constant during the change of state, the process is represented on the TS-plane by a straight line parallel to the S-axis, as AB, Fig. 16. Since T is constant, the change of entropy is given by

$$S_B - S_A = \frac{1}{T}\int_A^B dQ = \frac{{}_AQ_B}{T}.$$

That is, the change of entropy is simply the quotient of the heat absorbed (or rejected) by the system by the constant temperature.

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60. Adiabatic Changes.—In an adiabatic change $dQ = 0$, therefore

$$dS = \frac{dH}{T}.$$

If the process is frictionless $dH = 0$, $dS = 0$; that is, the entropy remains constant and the change is represented by a straight line parallel to the T-axis, as CD, Fig. 16. If the process involves the internal generation of heat H, then since dH must be positive, there must be an increase of entropy.

The two cases are illustrated by the expansion of steam (*a*) in a non-conducting cylinder; (*b*) in a steam turbine. The point A, Fig. 17, represents the initial condition of the steam in each case. The expansion in the cylinder of the reciprocating engine may be considered as frictionless and is therefore represented by the line AB parallel to the T-axis. In the turbine the steam passes through nozzles and blades and because of friction the internal generation of heat cannot be avoided. There is consequently an increase of entropy and the curve representing the process takes the course AC. The area $A_1 ACC_1$ represents the heat H thus generated.

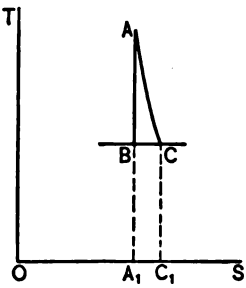


FIG. 17.

61. Cycle Processes.—A series of processes forming a closed cycle is represented on the TS-plane by a closed figure. The area included within the boundary represents the integral of TdS for the cycle; that is

$$\text{area} = (\int) TdS. \tag{1}$$

Now if the processes are all frictionless, we have for each

$$dQ = TdS,$$

whence $$(\int) TdS = (\int) dQ = (Q). \tag{2}$$

That is, the area of the cycle represents the heat absorbed by the system in traversing the cycle.

If we combine the two equations

$$dQ = TdS,$$
$$dQ = dU + ApdV,$$

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we obtain

$$TdS = dU + ApdV,$$

whence

$$(\int)TdS = (\int)dU + A(\int)pdV. \tag{3}$$

Since for a closed cycle the change of energy is zero, that is, $(\int)\, dU = 0$, we have

$$(\int)TdS = A(\int)pdV. \tag{4}$$

The first integral gives the heat absorbed, the second integral the work done by the system; hence

$$(Q) = A(W). \tag{5}$$

It follows that the area of a cycle on the TS-plane, provided there are no processes that involve friction, represents the work obtained from the system.

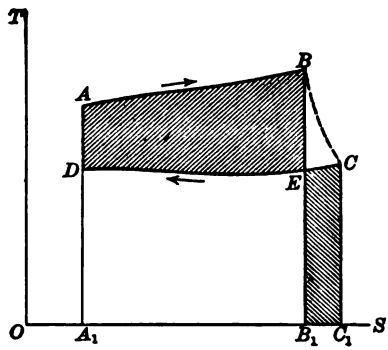


FIG. 18.

For the reversed cycle, (Q) and (W) are both negative. The system discharges the heat (Q) which is the equivalent of the external work (W) done on it.

Let us consider the case in which friction is involved in some of the processes. Thus in Fig. 18, suppose BC to represent an adiabatic expansion in which heat H(= area $B_1\, BCC_1$) is generated through friction. As before, the area of the cycle represents the integral $(\int)\, TdS$. But in this case

$$(\int)TdS = (Q) + (H). \tag{6}$$

From the energy equation we have, however, for all cases

$$(Q) = A(W);$$

hence

$$(\int)TdS = A(W) + (H)$$

or

$$A(W) = (\int)TdS - (H). \tag{7}$$

That is, the work obtained from the system is less than the work

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indicated by the area of the cycle by the equivalent of the heat H.

Referring to Fig. 18, the integral $(\int)TdS$ is represented by the cycle area $ABCD$, the heat H by the area B_1BCC_1, and therefore the heat transferred into work is represented by the difference

$$ABCD - B_1BCC_1 = ABED - B_1ECC_1.$$

The area $ABED$ represents the work that would have been obtained if the frictionless adiabatic had been followed; hence the area B_1ECC_1 represents the loss of work due to the irreversible process.

If the cycle is reversed the signs of $A(W)$ and $(\int)TdS$ are changed but the sign of H must remain unchanged. Equation (7) becomes for the reversed cycle

$$-A(W) = -(\int)TdS - (H). \tag{8}$$

In this case the work done on the system is larger than that indicated by the cycle area, the difference being the heat H.

62. The Rectangular Cycle. When the curves representing the four processes of the Carnot cycle are transferred to the TS-plane, the cycle becomes the simple rectangle $ABCD$, Fig. 19. The area A_1ABB_1 represents the heat Q_1 absorbed by the medium from the source during the isothermal expansion AB, and the area B_1CDA_1, the heat Q_2 rejected to the refrigerator during the isothermal compression CD. The lines BC and DA represent, respectively, the adiabatic expansion and the adiabatic compression.

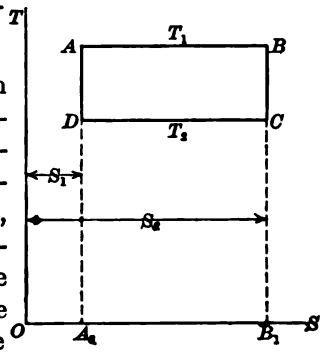


FIG. 19.

From the geometry of the figure, we have

$$Q_1 = T_1(S_2 - S_1),$$
$$Q_2 = T_2(S_2 - S_1),$$
$$A(W) = Q_1 - Q_2 = (T_1 - T_2)(S_2 - S_1),$$

whence

$$\eta = \frac{A(W)}{Q_1} = \frac{T_1 - T_2}{T_1}, \tag{1}$$

as already deduced.

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When the cycle is traversed in the counterclockwise sense, the heat Q_2 is received by the medium from the cold body during, the isothermal expansion DC, and the larger amount of heat Q_1 is rejected to the hot body during isothermal compression BA. The difference $Q_2 - Q_1 = -A(W)$ represented by the cycle area is the heat equivalent of the work that must be done *on* the medium, and must therefore be furnished from external sources.

The reversed heat engine may be used either as a refrigerating machine or as a warming machine. In the first case the space to be cooled acts as the source and delivers the heat Q_2 = area A_1DCB_1 to the medium. In the second case the space to be warmed receives the heat Q_1 area B_1BAA_1 from the medium.

EXAMPLE. A reversed Carnot engine is used for refrigeration. The temperature of the cold body (brine or cold room) is 12° F. and the temperature of the body to which heat is rejected (usually water) is 66°F. With the expenditure of 15 horse power, how much heat per minute will be taken from the cold body?

Since 1 horsepower-minute = 42.44 B. t. u., the work expended per minute is $42.44 \times 15 = 636.6$ B. t. u. This is represented by the area $ABCD$ of the cycle, Fig. 19. The heat absorbed from the cold body is represented by the area A_1DCB_1. Since the two rectangles in question have the same width, their areas are proportional to their vertical dimensions; thus

$$\frac{\text{Area } A_1DCB_1}{\text{Area } ABCD} = \frac{A_1D}{DA} = \frac{T_2}{T_2 - T_1};$$

or

$$\frac{Q_2}{636.6} = \frac{471.6}{66 - 12},$$

and

$$Q_2 = 636.6 \times \frac{471.6}{54} = 5676.1 \text{ B. t. u.}$$

The heat rejected is therefore

$$Q_1 = Q_2 + AW = 5676.1 + 636.6 = 6312.7 \text{ B. t. u.}$$

EXERCISES

1. The source has a temperature of 430° F. and the outside temperature is 40° F. Assume that the source is large so that the temperature is not affected by withdrawal of heat. If 450 B. t. u. be taken from source, what is the maximum work in foot pounds that may be obtained.

2. Let the temperature of source be 380° F., that of cold body 90° F. If another refrigerator can be found at a temperature of 38° F., by what per cent. is the available energy increased?

3. In Ex. 2 let the higher temperature be changed from 380° to 520°

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keeping the refrigerator at 90° F. Find the increase of the available energy. Ans. 27 per cent.

4. In a Carnot engine 2200 B. t. u. are absorbed from the source at a temperature of 530° F. Find the heat rejected and the efficiency of the engine for each of the following refrigerator temperatures:

$$t_0 = 40°, 70°, 130°, 220°, 810°.$$

5. A steam engine requires 13,500 B. t. u. per h.p.-hr. The temperature in boiler is 350° F., that in the condenser 116° F. Find the ratio of the efficiency of the actual engine to the efficiency of the Carnot engine for the same temperature limits. Ans. 0.652.

6. A tank contains 200 lb. of water at a temperature of 185° F. With an outside temperature of 40° F., find the available energy in the water. Take the specific heat of water as 1. Ans. 3540 B. t. u.

7. A vessel containing 250 lb. of water is heated from 40° to 190° F. Taking specific heat as 1, find (*a*) heat absorbed. With 40° F. as lowest available temperature, find (*b*) increase of unavailable energy (*c*) increase of available energy. Ans. (*c*) 4700 B. t. u.

8. In Ex. 7 heat is taken from gases of combustion at a temperature of 2040° F. Find the available energy of the heat Q required in (*a*) of Ex. 7, when that heat was contained in the gaseous system. Taking the water and gases as a single system, find the total change of available energy.
Ans. Loss = 25,300 B. t. u.

9. A vessel contains 80 lb. of water at 40°, which may be taken as lowest available temperature. The water is stirred by a paddle wheel until final temperature is 165°. (*a*) Find work required in foot pounds. (*b*) If a Carnot engine is used, with the water as a source and with 40° as the refrigerator temperature, what per cent of this work may be recovered?
Ans. (*b*) 11 per cent.

10. Let 20 lb. of water at 40° F. (the lowest available temperature) be mixed with 30 lb. of water at 190° F. Calculate the resulting change of available energy. Ans. 200 B. t. u. loss.

11. A 10-h.p. Carnot engine takes 120,000 B. t. u. per hour from a source at 340° F. Find the temperature of the refrigerator. Ans. 170° F.

12. A reversed Carnot engine is used for heating a building. The outside air at −10° F. is the cold body, the building at 70° F. is the hot body, and 200,000 B. t. u. per hour are required for heating. Find (*a*) heat taken from outside atmosphere per hour; (*b*) minimum horsepower required. Ans. (*b*) 11.9 h.p.

13. A reversed Carnot cycle is used for refrigeration. The temperature of the refrigerator is 0° F., that of the hot body 75° F. Find ideal h.p.

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required in order that 7000 B. t. u. per minute may be taken from the refrigerator. Find also heat discharged per minute into the hot body.

Ans. 27 h.p. nearly

14. A mass of air is compressed slowly and adiabatically, and in the process the work expended is 25,000 ft.-lb.

(*a*) What is the increase of energy of the air?
(*b*) How much of this is available energy?

15. 1 lb. of water at 60° enters a boiler and is heated to the boiling point, 360° F. It is then vaporized, and absorbs 863.6 B. t. u. during vaporization. With 40° F. as the lowest available temperature, calculate the increase of the available energy during heating and vaporization.

Ans. 411 B. t. u.

16. Find the increase of entropy when 3.5 lb. of air is heated from 60° to 450° F. (*a*) At constant volume; (*b*) at constant pressure.

17. The specific heat of nitrogen at constant pressure is given as $c_p = 0.2343 + 0.000021t$. Find the increase of entropy when 1 lb. is heated from 250° to 1400° F. Ans. 0.2407

18. A pound of water is vaporized in a boiler under a pressure of 160 lb. per sq. in. The water absorbs the latent heat of vaporization 860.5 B. t. u. and during the process the temperature remains constant at 363.6° F. (*a*) Find the increase of entropy during the process. (*b*) If the condenser temperature is 104° F., how much of the 860.5 B. t. u. is available energy? (*c*) How much is available if the lowest available temperature is 160° F.?

Ans. (*a*) 1.0453; (*b*) 271.4 B. t. u.; (*c*) 167.1 B. t. u.

19. Air is compressed from an initial pressure of 14.5 lb. to a pressure of 75 lb. per sq. in. according to the law $pv^{1.33} = \text{const.}$ The initial temperature is $t_1 = 60°$ F. (*a*) Find the temperature at the end of compression. (*b*) Find the change of entropy per pound of air, and on the *TS*-plane plot the curve representing the process.

SUGGESTION. The specific heat is $c_n = c_v \frac{k-n}{1-n}$ (see Art. 38), and $ds = c_n \frac{dT}{T}$.

Ans. (*a*) 321.6° F.; (*b*) − 0.01496

20. In the isothermal expansion of a gas (Art. 35) the external work is given by the expression

$$_1W_2 = MBT \log_e \frac{V_2}{V_1}.$$

Show that the expression for increase of entropy is

$$S_2 - S_1 = ABM \log_e \frac{V_2}{V_1}.$$

21. Show that this same expression gives the increase of entropy in the

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case of irreversible increase of volume, as in Joules experiment, Art. 31. What does the increase of entropy indicate in this case?

22. A reversed motor, rectangular cycle, operates between temperature limits of 10° and 130°, and receives 1800 B. t. u. per minute from the cold body. Find the heat rejected to the hot body, and the horsepower required to drive the motor.

23. A direct motor, rectangular cycle, operating between temperatures $T_1 = 900°$ and $T_2 = 680$, takes 1000 B. t. u. from a boiler. The heat rejected is delivered to a building for heating purposes. This direct motor drives a reversed motor which operates on a rectangular cycle between temperatures $T_4 = 460°$ (temperature of outside atmosphere) and $T_3 = 600$. The reversed motor takes heat from the atmosphere and rejects heat to the building. Find the total heat delivered to the building per 1000 B. t. u. taken from the boiler. Ans. 1803 B. t. u.

24. A ball of copper weighing 7 lb. and at a temperature of 850° F. is plunged into a vessel of water containing 40 lb. at a temperature of 60° F. Take the specific heat of copper as 0.095, that of water as 1. Find (*a*) the final temperature attained; (*b*) the total change of entropy of copper and water. Ans. (*a*) 72.92° F.; (*b*) +0.4015

25. Redraw Fig. 18 with the following specifications. AB is an isothermal $T_1 = 850$; CD is an isothermal, $T_2 = 530$; $S_A = S_D = 0.3$; $S_B = 1.4$; $S_C = 1.5$. The curve BC, as in Fig. 18, represents an irreversible adiabatic, such as is found in the case of expansion in the steam turbine. Find the heat converted into work: (*a*) If the irreversible adiabatic BC is followed; (*b*) if the reversible adiabatic BE is followed.

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CHAPTER VI

GENERAL EQUATIONS OF THERMODYNAMICS

63. Heat Absorbed During a Change of State.—A change of state of a system is generally accompanied by the absorption of heat from external sources. If we denote by q heat thus absorbed per unit weight, we may by giving q proper signs cover all possible cases; thus $+q$ indicates heat aborbed, $-q$ heat rejected; while if $q = 0$, we have the limiting adiabatic change of state.

The heat absorbed may be determined from the changes in two of the three variables p, v, t that define the state of the system. For example, let t and v be taken as the independent variables, and let the curve AB (Fig. 20) represent on the tv-plane a change of state. Suppose an element PR of this curve to be replaced by the broken line PQR, then the segment PQ represents an increment of volume Δv with t constant and the segment QR an increment of temperature Δt with v constant.

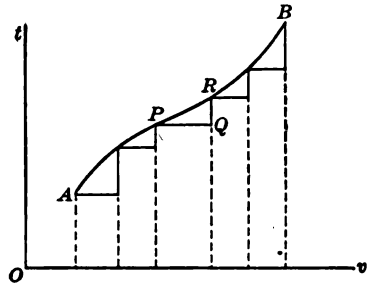


FIG. 20.

The *rate* of absorption of heat along PQ, that is, the heat absorbed per unit increase of volume, is denoted by the symbol $\left(\frac{\partial q}{\partial v}\right)_t$, the subscript t indicating that t is held constant during the process. If the rate of absorption be multiplied by the change of volume v, the product $\left(\frac{\partial q}{\partial v}\right)_t \Delta v$ is evidently the heat absorbed during the change of state represented by PQ. Similarly, the rate of absorption along QR is denoted by $\left(\frac{\partial q}{\partial t}\right)_v$ and the heat absorbed is the product $\left(\frac{\partial q}{\partial t}\right)_v \Delta t$. The heat absorbed during the change PQR is, therefore,

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$$\Delta q = \left(\frac{\partial q}{\partial v}\right)_t \Delta v + \left(\frac{\partial q}{\partial t}\right)_v \Delta t, \tag{1}$$

and the total heat absorbed along the broken path from A to B is given by the summation

$$\sum_{v_1,t_1}^{v_2,t_2}\left[\left(\frac{\partial q}{\partial v}\right)\Delta v + \left(\frac{\partial q}{\partial t}\right)\Delta t\right]. \tag{2}$$

By taking the elements into which the curve is divided smaller and smaller, the broken path may be made to approach the actual path between A and B. Therefore, passing to the limit, we have instead of (1)

$$dq = \left(\frac{\partial q}{\partial v}\right)_t dv + \left(\frac{\partial q}{\partial t}\right)_v dt, \tag{3}$$

and for the heat absorbed during the change of state

$$q = \int_{v_1,t_1}^{v_2,t_2}\left[\left(\frac{\partial q}{\partial v}\right)_t dv + \left(\frac{\partial q}{\partial t}\right)_v dt\right]. \tag{4}$$

By choosing other pairs of variables as independent, other equations similar to (3) may be obtained. Thus, taking t and p, we have

$$dq = \left(\frac{\partial q}{\partial t}\right)_p dt + \left(\frac{\partial q}{\partial p}\right)_t dp; \tag{5}$$

if p and v are chosen as the independent variables, we have the equation

$$dq = \left(\frac{\partial q}{\partial p}\right)_v dp + \left(\frac{\partial q}{\partial v}\right)_p dv. \tag{5}$$

64. Thermal Capacities.—The six coefficients $\left(\frac{\partial q}{\partial v}\right)_v, \left(\frac{\partial q}{\partial t}\right)_t$, etc. in equations (3), (5), and (6) are thermal capacities of the system. Each denotes the amount of heat required to change one of the independent variable by one unit when the other variable remains constant. Three of the coefficients have already received consideration (Art. 22) and have been given names and symbols.

$\left(\frac{\partial q}{\partial t}\right)_v$ is the specific heat at constant volume, denoted by c_v,

$\left(\frac{\partial q}{\partial t}\right)_p$ is the specific heat at constant pressure, denoted by c_p,

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$\left(\frac{\partial q}{\partial v}\right)_t$ is the latent heat of expansion, denoted by l_v.

The fourth coefficient $\left(\frac{\partial q}{\partial p}\right)_t$ may be denoted by l_p.

It should be observed that since q is not a point function of the variables p, v, t, these coefficients are *not* partial derivatives of a function.

65. Relations between Thermal Capacities.—Introducing the symbols c_v, c_p, l_v, and l_p in equations (3) and (5) of Art. 63, we have

$$dq = l_v dv + c_v dt, \tag{1}$$

$$dq = l_p dp + c_p dt. \tag{2}$$

By means of the characteristic equation of the substance, namely,

$$v = f(t,p), \tag{3}$$

various relations between the thermal capacities may be derived. Some of the most useful are the following.

From (3) we obtain by differentiation,

$$dv = \frac{\partial v}{\partial t} dt + \frac{\partial v}{\partial p} dp, \tag{4}$$

which substituted in (1) gives

$$dq = l_v \frac{\partial v}{\partial p} dp + \left(c_v + l_v \frac{\partial v}{\partial t}\right) dt. \tag{5}$$

Comparing (2) and (5), we have

$$l_p = l_v \frac{\partial v}{\partial p}, \tag{6}$$

$$c_p - c_v = l_v \frac{\partial v}{\partial t}. \tag{7}$$

In the same way, substituting

$$dp = \frac{\partial p}{\partial t} dt + \frac{\partial p}{\partial v} dv$$

in (2), and comparing the resulting equation with (1), we obtain

$$l_p = l_v \frac{\partial p}{\partial v}, \tag{8}$$

$$c_p - c_v = - l_p \frac{\partial p}{\partial t}. \tag{9}$$

The preceding relations connecting the thermal capacities of a system are independent of the first and second laws of

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thermodynamics and they would be valid even if the caloric theory of heat were accepted.

66. Relations Deduced from the Laws of Thermodynamics. The first law of thermodynamics is expressed by the energy equation

$$dq = du + Apv, \tag{1}$$

and the second law by the entropy equation

$$dq = Tds. \tag{2}$$

Through these laws the two magnitudes u and s have been introduced.

We now introduce a third thermal magnitude defined by the relation

$$i = u + Apv. \tag{3}$$

This new quantity i is one of the so-called *thermodynamic potentials* that are much used in the applications of thermodynamics to chemistry. We shall call it the **thermal potential** of the system, and for reasons that will appear later, we shall often call it the **thermal head**. Evidently i, like u, is a function of the state of the system and may be used as a coördinate. As shown by equations (1) and (3), both u and i are expressed in thermal units; if they are both expressed in mechanical units the defining relation is $i = u + pv$.

By differentiating (3) we obtain

$$di = du + Apdv + Avdp$$

or

$$di = dq + Avdp. \tag{4}$$

By a combination of equations (1), (2), and (4) with equations (1) and (2) of the preceding article, dq may be eliminated, and the differentials of u, i, and s may be expressed in terms of the coordinates p, v, T and the thermal capacities. The resulting expressions are:

$$du = (l_v - Ap)dv + c_v dT, \tag{5}$$

$$di = (l_p + Av)dp + c_p dT, \tag{6}$$

$$ds = \frac{l_v}{T}dv + \frac{c_v}{T}dT, \tag{7}$$

$$ds = \frac{l_p}{T}dp + \frac{c_p}{T}dT. \tag{8}$$

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Since u, i, and s are functions of the state, the differentials du, di, and ds are exact, and consequently the coefficients of dv, dp and dt in these four equations are partial derivatives. Thus

$$l_v - Ap = \left(\frac{\partial u}{\partial v}\right)_t, \quad c_v = \left(\frac{\partial u}{\partial T}\right)_v,$$

$$l_p + Av = \left(\frac{\partial i}{\partial p}\right)_t, \quad c_p = \left(\frac{\partial i}{\partial T}\right)_p,$$

$$\frac{l_v}{T} = \left(\frac{\partial s}{\partial v}\right)_t, \quad \frac{c_v}{T} = \left(\frac{\partial s}{\partial T}\right)_v,$$

$$\frac{l_p}{T} = \left(\frac{\partial s}{\partial p}\right)_t, \quad \frac{c_p}{T} = \left(\frac{\partial s}{\partial T}\right)_p.$$

Since
$$\frac{\partial}{\partial T}\frac{\partial u}{\partial v} = \frac{\partial}{\partial v}\frac{\partial u}{\partial T},$$

we have
$$\frac{\partial}{\partial T}(l_v - Ap) = \frac{\partial}{\partial v} c_v,$$

or
$$\frac{\partial l_v}{\partial T} - A\frac{\partial p}{\partial T} = \frac{\partial c_v}{\partial v}. \tag{9}$$

Likewise from the second pair of coefficients,

$$\frac{\partial l_p}{\partial T} + A\frac{\partial v}{\partial T} = \frac{\partial c_p}{\partial p}. \tag{10}$$

From the third pair of coefficients, we have

$$\frac{\partial}{\partial T}\left(\frac{l_v}{T}\right) = \frac{\partial}{\partial v}\left(\frac{c_v}{T}\right) \tag{11}$$

$$\frac{1}{T}\frac{\partial l_v}{\partial T} - \frac{l_v}{T^2} = \frac{1}{T}\frac{\partial c_v}{\partial v},$$

or
$$\frac{\partial l_v}{\partial T} - \frac{l_v}{T} = \frac{\partial c_v}{\partial v}. \tag{12}$$

Similarly from the fourth pair

$$\frac{\partial l_p}{\partial T} - \frac{l_p}{T} = \frac{\partial c_p}{\partial p}. \tag{13}$$

Combining (9) and (12), the result is the relation

$$\frac{l_v}{T} = A\frac{\partial p}{\partial T}, \tag{14}$$

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and likewise from (10) and (13)

$$\frac{l_p}{T} = -A\frac{\partial v}{\partial T}. \tag{15}$$

67. General Equations.—From the preceding relations certain important general equations may be deduced.

Let the expression for the thermal capacities l_v and l_p given by (14) and (15) be substituted in equation (1) and (2) of Art. 65. The resulting equations are

$$dq = c_v dT + AT\left(\frac{\partial p}{\partial T}\right)_v dv, \tag{I}$$

$$dq = c_p dT - AT\left(\frac{\partial v}{\partial T}\right)_p dp. \tag{II}$$

When the same expressions are substituted in (5) and (6) of Art. 66, the following equations are obtained.

$$du = c_v dT + A\left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right]dv, \tag{III}$$

$$di = c_p dT - A\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]dp. \tag{IV}$$

From equations (11) and (14) of the preceding article, we have

$$\frac{\partial}{\partial T}\left(\frac{l_v}{T}\right) = \frac{\partial}{\partial v}\left(\frac{c_v}{T}\right) = A\frac{\partial^2 p}{\partial T^2}$$

or

$$\left(\frac{\partial c_v}{\partial v}\right)_t = AT\left(\frac{\partial^2 p}{\partial T^2}\right)_v. \tag{V}$$

In the same way, using (15) we obtain the relation

$$\left(\frac{\partial c_p}{\partial p}\right)_t = -AT\left(\frac{\partial^2 v}{\partial T^2}\right)_p. \tag{VI}$$

Finally, let the expression for l_v given by (14), Art. 66, be substituted in (7), Art. 65. The result is the important relation

$$c_p - c_v = AT\frac{\partial v}{\partial T}\frac{\partial p}{\partial T}. \tag{VII}$$

68. Applications of the General Equations.—The equations (I) to (VII) are useful in the investigation of the properties of gases and vapors. If the characteristic equation of the substance is known, the various derivatives are readily obtained.

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(*a*) *Perfect Gases.*—The characteristic equation is

$$pv = BT,$$

from which,

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{B}{v}, \qquad \left(\frac{\partial v}{\partial T}\right)_p = \frac{B}{p}. \tag{1}$$

Inserting these expressions for the derivatives in (III) and (IV) respectively, we have

$$du = c_v dT + A\left[\frac{BT}{v} - p\right]dv = c_v dT, \tag{2}$$

$$di = c_p dT - A\left[\frac{BT}{p} - v\right]dp = c_p dT. \tag{3}$$

Since du and di are exact differentials it follows that $c_v dT$ and $c_p dT$ must be integrable; hence c_v and c_p, for a perfect gas, must be constants or functions of T only.

From equation (VII),

$$c_p - c_v = AT\frac{B}{p}\cdot\frac{B}{v} = AB. \tag{4}$$

Hence the difference between the specific heats is a constant.

From equation (2) it appears that the energy of a gas that follows the law $pv = BT$ depends on the temperature only; that is, it is all of the kinetic form.

If the expressions for the derivatives are substituted in the general equations (I) and (II) the resulting equations are

$$dq = c_v dT + AB\frac{T}{v}dv, \tag{5}$$

$$dq = c_p dT - AB\frac{T}{p}dp. \tag{6}$$

From these we have the equations

$$ds = c_v\frac{dT}{T} + AB\frac{dv}{v}, \tag{7}$$

$$ds = c_p\frac{dT}{T} - AB\frac{dp}{p}, \tag{8}$$

from which expressions for the entropy of the gas may be obtained. Integrating (7) with c_v constant, we have

$$s = c_v \log_e T + AB \log_e v + s_0, \tag{9}$$

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or for a change of state

$$s_2 - s_1 = c_v \log_e \frac{T_2}{T_1} + AB \log_e \frac{v_2}{v_1}. \tag{10}$$

Similarly, from (8)

$$s_2 - s_1 = c_p \log_e \frac{T_2}{T_1} - AB \log_e \frac{p_2}{p_1}. \tag{11}$$

Eliminating $\frac{T_2}{T_1}$ between (10) and (11), we get a third expression, namely

$$s_2 - s_1 = c_p \log_e \frac{v_2}{v_1} + c_v \log_e \frac{p_2}{p_1}. \tag{12}$$

(*b*) *Van der Waals' Equation.* Certain so-called imperfect gases, as carbonic acid, follow the equation of van der Waals, namely

$$p = \frac{BT}{v - b} - \frac{a}{v^2}.$$

By the application of the general equations we endeavor to gain some information regarding the properties of such gases.

By differentiation of the characteristic equation we obtain

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{B}{v - b}, \qquad \frac{\partial^2 p}{\partial T^2} = 0, \tag{13}$$

$$T\left(\frac{\partial p}{\partial T}\right)_v - p = \frac{BT}{v - b} - p = \frac{a}{v^2}. \tag{14}$$

Introducing these expression in (I), (III), and (V), we have

$$dq = c_v dT + \frac{ABT}{v - b} dv, \tag{15}$$

$$du = c_v dT + \frac{Aa}{v^2} dv, \tag{16}$$

$$\frac{\partial c_v}{\partial v} = 0. \tag{17}$$

From (17) it appears that c_v is independent of the volume and from (16) it is evident that c_v must be a constant or function of the temperature only, and therefore independent of the pressure also.

If c_v is taken as constant, integration of (16) gives for the change of energy between two states

$$u_2 - u_1 = c_v(T_2 - T_1) + Aa\left(\frac{1}{v_1} - \frac{1}{v_2}\right). \tag{18}$$

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Thus the gas experiences a change of potential energy due to its change of volume as well as a change of kinetic energy due to the change of temperature.

To get an expression for the change of entropy we divide both members of (15) by T; thus

$$ds = \frac{dq}{T} = c_v \frac{dT}{T} + AB \frac{dv}{v - b}. \tag{19}$$

Taking c_v as constant, and integrating this expression, we have

$$s_2 - s_1 = c_v \log_e \frac{T_2}{T} + AB \log_e \frac{v_2 - b}{v_1 - b}. \tag{20}$$

(*c*) *Superheated Steam.* One of the important questions in the investigation of the properties of super heated steam is the variation of the specific heat c_p. If a proper characteristic equation is known, the general equation (VI) offers a means of attacking this problem.

The most reliable experiments on the volume of superheated steam are represented quite accurately by the equation

$$v - c = \frac{BT}{p} - (1 + 3ap^{\frac{1}{3}}) \frac{m}{T^n}, \tag{21}$$

in which B, a, m, n, and c are constants. Successive differentiation of this equation gives the derivatives

$$\frac{\partial v}{\partial T} = \frac{B}{p} + (1 + 3ap^{\frac{1}{3}}) \frac{mn}{T^{n+1}},$$

$$\frac{\partial^2 v}{\partial T^2} = - (1 + 3ap^{\frac{1}{3}}) \frac{mn(n + 1)}{T^{n+2}}.$$

Substituting the second derivative in equation (VI), the result is

$$\left(\frac{\partial c_p}{\partial p}\right)_T = (1 + 3ap^{\frac{1}{3}}) \frac{Amn(n + 1)}{T^{n+1}}. \tag{22}$$

Since the expression given by (22) is necessarily positive in sign, it follows that the specific heat c_p must increase with the pressure when the temperature is held constant.

Integration of (22) with T constant gives the equation

$$c_p = p(1 + 2ap^{\frac{1}{3}}) \frac{Amn(n + 1)}{T^{n+1}} + \varphi(T), \tag{23}$$

in which $\varphi(T)$ is a function of the temperature that must be determined by experiment. With this function known, (23) gives the specific heat as a function of the pressure and temperature.

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69. Significance of the Thermal Potential.—Referring to Art. 66, let us consider equations (1) and (4), namely

$$du = dq - Apdv, \tag{1}$$

$$di = dq + Avdp. \tag{2}$$

For a constant-volume process (1) becomes

$$du = dq$$

or

$$u_2 - u_1 = {}_1q_2. \tag{3}$$

Similarly, for a change of state at constant pressure, (2) becomes

$$di = dq$$

or

$$i_2 - i_1 = {}_1q_2. \tag{4}$$

It is seen that the thermal potential i bears the same relation to a constant pressure process that the intrinsic energy u does to a constant volume process. In general, i is associated with p in the same way that u is associated with v.

Changes of state at constant pressure are important especially in connection with vapors. For example, the heating of water in a boiler, the vaporization of the water, the superheating, and finally the condensation of the steam occur under constant pressure. Equation (4) expresses the fact that with the pressure constant *the heat absorbed is the difference between the initial and final values of the potential i.*

70. Thermodynamic Potentials.—Since the magnitudes p, v, T, u, and s are functions of the state of the system, any combination of them is also a function of the state. One such function is the thermal potential

$$i = u + Apv \tag{1}$$

introduced in Art. 66. Two other functions that are useful in certain applications of thermodynamics to chemistry are the following:

$$F = u - Ts, \tag{2}$$

$$\Phi = u - Ts + Apv. \tag{3}$$

The three functions defined by (1), (2), and (3) are called **thermodynamic potentials.**

Making use of the energy equation

$$dq = du + Apdv$$

and the entropy equation

$$dq = Tds,$$

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which holds for frictionless reversible processes, the following expressions are found for the differentials of the three thermodynamic potentials:

$$di = Tds + Avdp; \tag{4}$$

$$-dF = sdT + Apdv, \tag{5}$$

$$d\Phi = Avdp - sdT. \tag{6}$$

Thus by differentiating (3) we have

$$\begin{aligned} d\Phi &= du - d(Ts) + Ad(pv) \\ &= du - Tds - sdT + Apdv + Avdp. \end{aligned}$$

But $du + Apdv - Tds = 0$, and therefore

$$d\Phi = -sdT + Avdp.$$

Certain results follow immediately from (4), (5), and (6). For example, for an isothermal expansion (5) becomes

$$-dF = Apdv,$$

whence $$-\int_1^2 dF = A\int_{v_1}^{v_2} pdv$$

or $$A\,{}_1W_2 = F_1 - F_2,$$

that is, the external work obtained is equal to the decrease of the potential F.

71. Equilibrium.—The equation $dq = Tds$ holds good only for frictionless reversible processes. If the process is irreversible we have the inequality

$$dq < Tds. \qquad \text{[See Eq. (3), Art. 57]} \tag{1}$$

Hence for such processes the equations (4), (5), and (6) of the preceding article are replaced by the inequalities

$$di < Tds + Avdp, \tag{2}$$

$$-dF > sdT + Apdv, \tag{3}$$

$$d\Phi < Avdp - sdT. \tag{4}$$

From the inequalities (3), (4), and (1) the following conclusions are at once apparent:

1. If the temperature and volume of a system remain constant, then from (3), $dF < 0$. That is, dF must be negative, and any change in the system must result in a decrease of the function F.

2. If the temperature and pressure remain constant, as in fusion and vaporization, then from (4), $d\Phi < 0$. Hence any change in the system must be such as to decrease the function Φ.

3. If the system be isolated, $q = 0$, and from (1), $ds > 0$. Hence in an isolated system any change must result in an increase of entropy.

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The conditions of equilibrium are readily deduced from these conclusions. Under the condition of constant T and v, change is possible so long as F can decrease. When F becomes a minimum, no further change is possible and the system is in stable equilibrium. Likewise, with T and p constant, stable equilibrium is attained when the function Φ is a minimum.

The functions F and Φ are evidently analogous to the potential function V in mechanics. A mechanical system is in a state of equilibrium when the potential energy is a minimum, and similarly a thermodynamic system is in equilibrium when either the function F or the function Φ is a minimum. For this reason F and Φ are called thermodynamic potentials.

By the use of thermodynamic potentials, problems relating to fusion, vaporization, solution, chemical equilibrium, etc., are attacked and solved.

EXERCISES

1. If the characteristic equation of a substance is $pv = BT - Cp^n$, show that the difference of specific heats is given by the expression

$$c_p - c_v = \frac{AB}{1 + (n-1)\frac{Cp^n}{BT}}.$$

2. Using the general equation (VI), show that the specific heat at constant pressure of a substance obeying the preceding characteristic equation cannot vary with the pressure.

3. Callendar's equation for superheated steam is

$$p(v - b) = bT - \frac{Cp}{T^n}$$

Show that c_p must be a function of p and T.

4. In the equations of Art. 70, namely,

$$du = Tds - Apdv \qquad di = Tds + Avdp$$
$$-dF = sdT + Apdv \qquad d\Phi = -sdT + Avdp,$$

the differentials are exact, since u, i, F, and Φ are point functions. Apply the test of exactness and derive Maxwell's relations, which are

$$\left(\frac{\partial T}{\partial v}\right)_s = -A\left(\frac{\partial p}{\partial s}\right)_v, \qquad \left(\frac{\partial T}{\partial p}\right)_s = A\left(\frac{\partial v}{\partial s}\right)_p,$$
$$\left(\frac{\partial s}{\partial v}\right)_T = A\left(\frac{\partial p}{\partial T}\right)_v, \qquad \left(\frac{\partial s}{\partial p}\right)_T = -A\left(\frac{\partial v}{\partial T}\right)_p.$$

5. Deduce (V) from (III), and also (VI) from (IV).

SUGGESTION. The differentials du and di are exact; hence apply the test for exactness.

6. Derive (V) and (VI) by the following method. Divide both members of (I) and (II) by T, and knowing that $\frac{dq}{T} = ds$ is exact, apply the criterion of exactness to the two differentials.

7. Deduce the following relations between the specific heats and the thermodynamic potentials F and Φ.

$$c_v = -T\frac{\partial^2 F}{\partial T^2}; \qquad c_p = \frac{\partial^2 \Phi}{\partial T^2}.$$

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CHAPTER VII

PROPERTIES OF VAPORS

72. The Process of Vaporization.—The term vaporization may refer either to the slow and quiet formation of vapor at the free surface of a liquid or to the formation of vapor by ebullition. In the latter case, heat being applied to the liquid, the temperature rises until at a definite point vapor bubbles begin to form on the walls of the containing vessel and within the liquid itself. These rise to the liquid surface, and breaking, discharge the vapor contained in them. The liquid, meanwhile, is in a state of violent agitation. If this process takes place in an inclosed space—as a cylinder fitted with a movable piston—so arranged that the pressure may be kept constant while the inclosed volume may change, the following phenomena are observed:

1. With a given constant pressure, the temperature remains constant during the process; and the greater the assumed pressure, the higher the temperature of vaporization. The temperature here referred to is that of the vapor above the liquid. As a matter of fact, the temperature of the liquid itself is slightly greater than that of the vapor, but the difference is small and negligible.

2. At a given pressure a unit weight of vapor assumes a definite volume, that is, the vapor has a definite density; and if the pressure is changed, the density of the vapor changes correspondingly. The density (or the specific volume) of a vapor is, therefore, a function of the pressure.

3. If the process of vaporization is continued at constant pressure until all the liquid has been changed to vapor, then if heat be still added to the vapor alone, the temperature will rise and the specific volume will increase; that is, the density will decrease.

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So long as any liquid is present the vapor has a constant maximum density and a constant temperature. The vapor in this case is said to be **saturated** and the constant temperature corresponding to the pressure at which the process is carried on is the **saturation temperature.** If no liquid is present, and through absorption of heat the temperature of the vapor rises above the saturation temperature, the vapor is said to be **superheated.** The difference between the temperature of the vapor and the saturation temperature is called the **degree of superheat.**

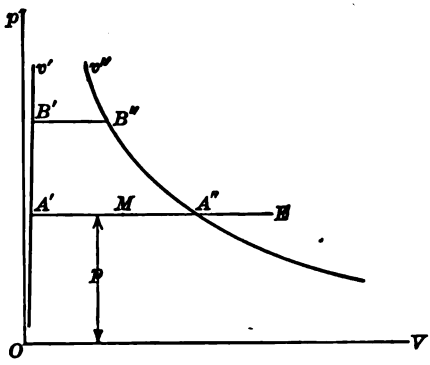


FIG. 21.

The process of vaporization may be represented graphically on the pV-plane. (Fig. 21.) Consider a unit weight of liquid subjected to a pressure p represented by the ordinate of the line $A'A''$; and let the volume of the liquid (denoted by v') be represented by A'. As vaporization proceeds at this constant pressure, the volume of the mixture of liquid and vapor increases, and the point representing the state of the mixture moves along the line $A'A''$. The point A'' represents the volume v'' of the saturated vapor at the completion of vaporization; therefore, the segment $A'A''$ represents the increase of volume $v'' - v'$. Any point between A' and A'', as M, represents the state of a mixture of liquid vapor, and the position of the point depends on the ratio of the weight of the vapor to the weight of the mixture. Denoting this ratio by x, we have $x = \frac{A'M}{A'A''}$, whence it appears that at A', $x = 0$, while at A'', $x = 1$. The ratio x is called the **quality** of mixture.

If the mixture is subjected to higher pressure during vaporization, the state-point will move along some other line, as $B'B''$. The specific volume indicated by B'' is smaller than that indicated by A''. The curve v'', giving the specific volumes of the saturated vapor for different pressures, is called the **saturation curve;**

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while the curve v', givng the corresponding liquid volume, is the **liquid curve.** These curves v', v'' are, in a sense, boundary curves. Between them lies the region of liquid and vapor mixtures, and to the right of v'' is the region of superheated vapor. Any point in this latter region, as E, represents a state of the superheated vapor.

73. Functional Relations. Characteristic Surfaces.—For a mixture of liquid and saturated vapor, the functional relations connecting the coördinates p, v, and t are essentially different from the relation for a permanent gas. As stated in the preceding article, the temperature of the mixture depends upon the pressure only, and we cannot, as in the case of a gas, give p and t independently any values we choose. The volume of a unit weight of the mixture depends (1) upon the specific volume of the vapor for the given pressure and (2) upon the quality x. Hence we have for a mixture the following functional relations:

$$t = f(p), \text{ or } p = F(t), \qquad (1)$$

$$v = \phi(p, x). \qquad (2)$$

With superheated steam, as with gases, p and t may be varied independently, and consequently the functional relation between p, v, and t has the general form

$$v = \psi(p,T) \qquad (3)$$

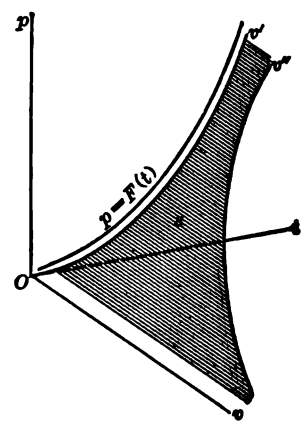


FIG. 22.

The characteristic surface of a saturated vapor is shown in Fig. 22. It is a cylindrical surface s whose generating elements cut the pt-plane in the curve $p = F(t)$. These elements are limited by the two space curves v' and v'', which when projected on the pv-plane give the curves v', v'' of Fig. 21. The space curve v'' is the intersection of the surface s and the surface for the superheated vapor.

74. Energy Equation applied to the Vaporization Process. It is customary in estimating the energy, entropy, and thermal potential of a saturated vapor to assume liquid at 32° F. (0° C.) as a datum from which to start. Thus the energy of a pound of

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steam is assumed to be the energy above that of a pound of water at 32° F.

Suppose that one pound of liquid at 32° is heated until its temperature reaches the boiling point corresponding to the pressure to which the liquid is subjected. The heat required is given by the equation

$$q' = \int_{32}^{t} c'dt, \tag{1}$$

where c' denotes the specific heat of the liquid. This process is represented on the Ts-plane by a curve AA' (Fig. 23). The ordinate OA represents the initial absolute temperature $32 + 459.6 = 491.6$, the ordinate A_1A' the temperature of vaporization given by the relation $t = f(p)$, and the area $OAA'A_1$ the heat q' absorbed by the liquid. This heat q' is called the **heat of the liquid.***

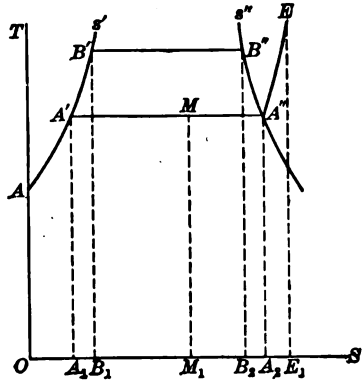


FIG. 23.

When the temperature of vaporization is reached, the liquid begins to change to vapor, the temperature remaining constant during the process. A definite quantity of heat, dependent upon the pressure, is required to change the liquid completely into vapor. This is called the **heat of vaporization** and is denoted by the symbol r. In Fig. 23, the passage of the statepoint from A' to A'' represents the vaporization, and the heat r is represented by the area $A_1A'A''A_2$. For a higher pressure the curve AB' represents the heating of the liquid and the line $B'B''$ the vaporization.

During the heating of the liquid the change in volume is very small and may be neglected; hence, the external work done is negligible also, and substantially all of the heat q' goes to increase the energy of the liquid. During vaporization, however, the volume changes from v' (volume of 1 lb. of liquid) to v'' (volume

*Symbols with primes, c', q', v', s', etc., are used for the liquid; symbols with double primes, c'', q'', v'', s'', etc., for the saturated vapor.

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of 1 lb. of saturated vapor). Since the pressure remains constant, the external work that must be done to provide for the increase of volume is

$$L = p(v'' - v'). \tag{2}$$

According to the energy equation, the heat r added during vaporization is used in increasing the energy of the system and in doing external work. Hence, the difference

$$r - AL = r - Ap\,(v'' - v') \tag{3}$$

is the heat required to increase the energy of the unit weight of substance when it changes from liquid to vapor. This heat is denoted by ρ and is called the **internal latent heat.** Since during the vaporization the temperature is constant, there is no change of kinetic energy; it follows that ρ is expended in increasing the potential energy of the system. The heat equivalent of the external work, namely $Ap(v'' - v')$, is called the **external latent heat,** and for convenience may be denoted by ψ. We have then

$$r = \rho + \psi. \tag{4}$$

The **total heat** of the saturated vapor is the sum of the heat of the liquid and the heat of vaporization. Thus,

$$q'' = q' + r,$$

or

$$q'' = q' + \rho + \psi. \tag{5}$$

In Fig. 23 the total heat is represented by the area $OAA'A''A_2$. Comparing (5) with the general energy equation, it is evident that the sum $q' + \rho$ gives the increase of energy of the saturated vapor over the energy of the liquid at 32° F. Denoting this by u'', we have

$$u'' = q' + \rho. \tag{6}$$

If heat is added at constant pressure after vaporization the vapor becomes superheated and the process is represented on the Ts-plane by the curve $A''E$, Fig. 23. The heat added is represented by the area $A_2A''EE_1$. The volume of the vapor is increased; therefore part of the heat added is expended in external work and the remainder goes to increase the energy of the vapor.

75. Thermal Potential of a Vapor.—The three changes represented by AA', $A'A''$, and $A''E$, Fig. 23, namely, heating the

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liquid, vaporization, and superheating, proceed at constant pressure; consequently the heat absorbed in any of the changes is equal to the increase in thermal potential (Art. 69).

Let i'_0, i', and i'' denoted respectively the values of the thermal potentials in the states represented by points A, A', A''; then for the heating of the liquid (AA') we have

$$q' = i' - i_0', \tag{1}$$

for the vaporization ($A'A''$)

$$r = i'' - i', \tag{2}$$

and for both processes

$$q'' = q' + r = i'' - i_0'. \tag{3}$$

If i_e is the potential of the superheated vapor in the state represented by point E the heat absorbed in superheating is $i_e - i''$, and the total heat absorbed between states A and E is $i_e - i_0'$. It is seen that for any state between A and E the thermal potential exceeds the heat absorbed by i_0', the thermal potential of the liquid at 32° F.

By definition we have for the thermal potential in this initial state

$$i_0' = u_0' + Apv_0, \tag{4}$$

in which u_0 denotes the intrinsic energy and v_0 the volume in this state.

It is customary to take the liquid at 32° F. as a zero point for energy and entropy; that is, for this state the energy u and entropy s are arbitrarily taken as zero. With $u'_0 = 0$, (4) becomes

$$i'_0 = Apv_0. \tag{5}$$

The physical significance of i'_0 is apparent. To force one pound of liquid having the volume v_0 into a boiler against the pressure p requires the work pv_0; hence i'_0 is the heat equivalent of the work of pumping the liquid into the boiler. We may say therefore that q'' is the heat expended in getting the fluid from state A to state A'' when the liquid is in the boiler at the start, while i'' is the energy required for the same purpose when the liquid is initially outside the boiler.

Except at very high pressures the numerical value of i'_0 is

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small. Thus for water $v_0 = 0.016$, and for a pressure of 100 lb. per sq. in.

$$i'_0 = \frac{144 \times 100 \times 0.016}{778} = 0.3 \text{ B. t. u.}$$

At the lower pressures, therefore, q' and i', or q'' and i'', may be considered as practically identical. Modern tables of the properties of vapors give i' and i'' rather than q' and q''.

76. Entropies. The initial entropy of the liquid at 32° F. is arbitrarily taken as zero, and the increase of entropy during the heating of the liquid is called the entropy of the liquid and is denoted by s'. Thus in Fig. 23, OA_1 represents the entropy s' of the liquid in the state A'. Denoting by c' the specific heat of the liquid, we have

$$ds' = \frac{dq'}{T} = \frac{c'dT}{T}$$

and

$$s' = \int_{491.6}^{T} c' \frac{dT}{T}.$$

Having c' expressed as a function of T, values of s' for various values of T may be calculated, and these when plotted give the curve s' called the **liquid curve.**

During the vaporization process the heat r is absorbed at the constant temperature T; hence the increase of entropy, represented by A_1A_2, is the quotient $\frac{r}{T}$. The entropy of the saturated vapor in the state A' is denoted by s''; hence

$$s'' = s' + \frac{r}{T}. \tag{2}$$

Values of s'' thus obtained when plotted give the curve s'', which is called the **saturation curve.**

In the superheating process $A''E$ there is a further increase of entropy. Denoting by T_1 and T_2 the absolute temperatures at A'' and E, respectively, and by c_p the specific heat of the superheated vapor at constant pressure, we have for the heat absorbed

$$i_e - i'' = \int_{T_1}^{T_2} c_p dT, \tag{3}$$

and for the increase of entropy

$$s_e - s'' = \int_{T_1}^{T_2} \frac{c_p dT}{T}. \tag{4}$$

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77. Properties of a Mixture.—A point lying between the curves s' and s'', as point M, Fig. 23, represents a mixture of liquid and vapor. The ratio between the segments $A'M$ and $A'A''$ gives the quality x of the mixture. In the change of state represented by $A'A''$ the thermal quantities that come under consideration are: latent heat r, increase of energy ρ, increase of entropy r/T, increase of volume $v''-v'$. Evidently for the change of state represented by $A'M$, the heat added is xr, the increase of energy is $x\rho$, the increase of entropy is xr/T, and the increase of volume is $x(v'' - v')$. Denoting the various quantities at state M by the subscript m, we have therefore

$$q_m = q' + xr, \tag{1}$$

$$i_m = i' + xr, \tag{2}$$

$$u_m = u' + x\rho, \tag{3}$$

$$s_m = s' + \frac{xr}{T}, \tag{4}$$

$$v_m = v' + x(v'' - v'). \tag{5}$$

When, as is usually the case, the point M is near the curve s'', more convenient expressions may be obtained by subtracting from values at the saturation limit. For example, at A'' the energy is u'' and at M the energy is less by the energy stored between M and A'', which is $(1 - x)\rho$; hence the energy in state M is given by the expression

$$u_m = u'' - (1 - x)\rho. \tag{3'}$$

Similarly

$$i_m = i'' - (1 - x)r, \tag{2'}$$

and

$$s_m = s'' - (1 - x)\frac{r}{T}. \tag{4'}$$

The expression (5) for the volume may be given the form

$$v_m = xv'' + (1 - x)v' \tag{5'}$$

Since, however, v' is small compared with v'' and the factor $(1 - x)$ is also usually small the product may be neglected and for all practical purposes we may assume that xv'' gives the volume of the mixture.

EXAMPLE. Find the properties of a mixture of steam and water at a pressure of 160 lb. per sq. in. with $x = 0.97$.

The properties of saturated steam at this pressure are*: $i'' = 1195.7$

* Properties of Steam and Ammonia, p. 34.

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$r = 860.5$, $\rho = 776.9$, $u'' = 1111.5$, $r/T = 1.0453$, $s'' = 1.5649$, $v'' = 2.839$
Hence

$$i_m = 1195.7 - (1 - 0.97)860.5 = 1169.9 \text{ B. t. u.}$$
$$u_m = 1111.5 - 0.03 \times 776.9 = 1088.2 \text{ B. t. u.}$$
$$s_m = 1.5649 - 0.03 \times 1.0453 = 1.5335$$
$$v_m = 2.839 \times 0.97 = 2.754 \text{ cu. ft.}$$

78. The Clapeyron Relation.—The various properties of a vapor are not independent but connected by certain relations deduced from the laws of thermodynamics. Thus the Clausius relation

$$\left(\frac{\partial c_p}{\partial p}\right)_t = -AT\frac{\partial^2 v}{\partial T^2} \qquad \text{(Art. 67)}$$

establishes a connection between the specific heat c_p and volume v of the superheated vapor. Another important relation first deduced by Clapeyron connects the latent heat r and the increase of volume $v'' - v'$ during vaporization. By definition the latent heat of expansion for this process is

$$l_v = \frac{r}{v'' - v'},$$

whence $$r = l_v(v'' - v'). \qquad \text{(Art. 24)} \qquad (1)$$

But for any change of state [Art. 66, Eq. (4)]

$$l_v = AT\frac{\partial p}{\partial T}. \qquad (2)$$

We have therefore

$$r = AT\frac{\partial p}{\partial T}(v'' - v'), \qquad (3)$$

which is Clapeyron's relation. The derivative $\frac{dp}{dt}$ is obtained from the equation $p = f(t)$ which connects the pressure and temperature of the saturated vapor.

Clapeyron's equation is useful in the computation of tables of the properties of a saturated vapor. If the pressure-temperature relation $p = f(t)$ is known, the derivative for any temperature is determined; then if values of r have been found experimentally the values of v'' may be calculated, or if v'' is known from experiment the equation may be used to calculate r.

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Saturated and Superheated Steam

79. Pressure-Temperature Relation.—The early experiments of Regnault on the corresponding temperatures and pressures of saturated steam have in recent years been reinforced by three sets of accurate experiments conducted, respectively, by Scheel and Heuse, Holborn and Henning, and Holborn and Baumann. The three sets cover the range of temperature from 32° F. to the critical temperature.

The following empirical formula represents with considerably accuracy these experiments throughout the entire range.

$$\log p = A - \frac{B}{T} - C \log T - DT + ET^2 - \Delta, \qquad (A)$$

in which

$$\Delta = 0.00002\left[10 - 10\left(\frac{t - 370}{100}\right)^2 + \left(\frac{t - 370}{100}\right)^4\right].$$

The constants are:

$A = 10.568808$ $\qquad$ $\log D = \bar{3}.6088020$

$\log B = 3.6881209$ $\qquad$ $\log E = \bar{6}.1463000$

$C = 0.0155$ $\qquad$ $T = t + 459.6$

80. Derivative $\frac{dp}{dT}$.—Upon differentiating the preceding equation we obtain

$$\frac{1}{p}\frac{dp}{dT} = 2.3026\left[\frac{B}{T^2} - D + 2ET - \frac{d\Delta}{dT}\right] - \frac{C}{T}$$

and

$$\frac{T}{p}\frac{dp}{dT} = 2.3026\left[\frac{B}{T} - DT + 2ET^2 - T\frac{d\Delta}{dT}\right] - C. \qquad (B)$$

This expression (B) will be useful in subsequent developments.

81. Steam Volumes. Characteristic Equation.—The most reliable experiments on the specific volume of saturated and superheated steam are those of Knoblauch, Linde and Klebe. These experiments are represented satisfactorily by the empirical equation

$$v - c = \frac{BT}{p} - (1 + 3ap^1)\frac{m}{T^n}. \qquad (C)$$

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With p in pounds per square inch the following are the values of the constants

$$\begin{aligned} \log B &= \bar{1}.77448 \\ \log m &= 10.82500 \\ \log 3a &= \bar{2}.71000 \\ n &= 4 \end{aligned}$$

The term c is not strictly a constant, though it may be so considered for practical purposes. It is the volume v' of the water corresponding to the pressure p. Hence, when the equation is used to determine the volume v'' of saturated steam, the first member is $v'' - v'$, that is, the increase of volume during vaporization.

82. Specific Heat of Superheated Steam.—The application of the general equation (VI)to equation (C) leads immediately to a general equation for the specific heat of superheated steam. See Art. 68 (c). Thus

$$c_p = \varphi(T) + \frac{Amn(n+1)}{T^{n+1}} p(1 + 2ap^{\frac{1}{2}}).$$

If the arbitrary function $\varphi(T)$ is given the form

$$\varphi(T) = \alpha + \beta T + \frac{\gamma}{T^2},$$

it is found that by a proper choice of constants the equation represents quite accurately the experiments of Knoblauch and Mollier. The final form of the equation is therefore

$$c_p = \alpha + \beta T + \frac{\gamma}{T^2} + \frac{Amn(n+1)}{T^{n+1}} p(1 + 2ap^{\frac{1}{2}}). \qquad (D)$$

The constants have the following values:

$$\begin{aligned} \alpha &= 0.320 \\ \beta &= 0.000126 \\ \gamma &= 23583 \end{aligned}$$

The constants a, m, and n are those of the characteristic equation.

Curves showing the variation of specific heat with temperature at various constant pressures are shown in Fig. 24. It is seen that the value of c_p decreases at first, reaches a minimum, and

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then increases again. At the higher temperatures the curves approach each other more closely, and, as shown by the equation, they all approach the curve $c_p = \varphi(T)$ as an asymptote when the temperature is extremely high.

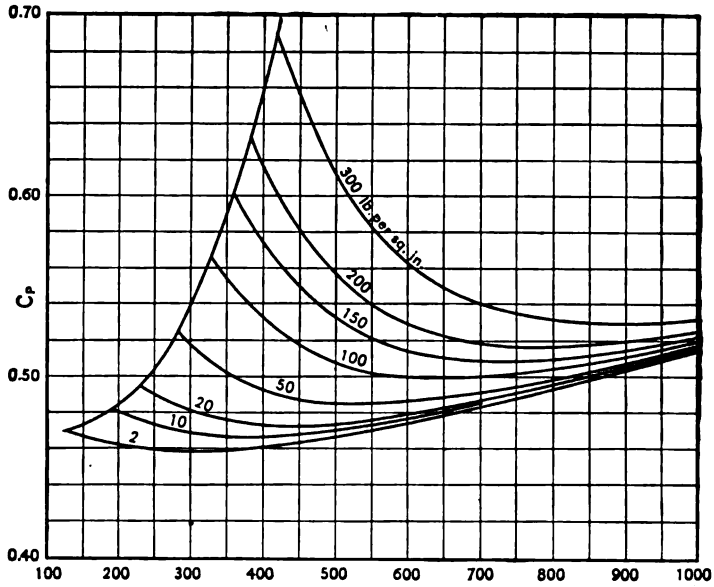


FIG. 24.

83. Thermal Potential.—In the general equation (IV), Art. 67, namely

$$di = c_p dT - A\left[T\left(\frac{\partial v}{\partial t}\right)_p - v\right]dp, \tag{1}$$

we introduce the expression for c_p given by (D) and from the characteristic equation (C) we obtain the term in the bracket. Thus

$$v = \frac{BT}{p} - (1 + 3ap^{\frac{1}{3}})\frac{m}{T^n} + c \tag{2}$$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{B}{p} + (1 + 3ap^{\frac{1}{3}})\frac{mn}{T^{n+1}} \tag{3}$$

$$T\left(\frac{\partial v}{\partial T}\right)_p = \frac{BT}{p} + (1 + 3ap^{\frac{1}{3}})\frac{mn}{T^n} \tag{4}$$

$$T\left(\frac{\partial v}{\partial T}\right)_p - v = (1 + 3ap^{\frac{1}{3}})\frac{m(n+1)}{T^n} - c. \tag{5}$$

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Making these substitutions (1) becomes

$$di = \left[\alpha + \beta T + \frac{\gamma}{T^2} + \frac{Amn(n+1)}{T^{n+1}} p(1 + 2ap^{\frac{1}{2}})\right] dT - A\left[\frac{m(n+1)}{T^n}(1 + 3ap^{\frac{1}{2}}) - c\right] dp. \quad (6)$$

Equation (6) is exact and its integration gives the following equation for the thermal potential i:

$$i = \alpha T + \tfrac{1}{2}\beta T^2 - \frac{\gamma}{T} - \frac{Am(n+1)}{T^n} p(1 + 2ap^{\frac{1}{2}}) + Acp + i_0. \quad (E)$$

If corresponding values of p and T for the saturation condition are substituted in (E) the thermal potential i'' of saturated steam at this pressure and temperature is obtained. The constant i_0 is found from the value of i'' at 212° F., which by experiment is known to be 1151.7 B. t. u. In this way the value $i_0 = 948.54$ B. t. u. is determined.

In using equation (E) for computation the matter of consistent units must receive careful attention. In the parenthesis $(1 + 2ap^{\frac{1}{2}})$ the value of the constant a presupposes that p is taken in pounds for square inch; elsewhere the pressure must be taken in pounds per square *foot*. It is convenient, however, to consider the pressures in pounds per square inch throughout, which is permissible provided the terms that involve p are multiplied by 144. The equation may therefore be given the form

$$i = \alpha T + \tfrac{1}{2}\beta T^2 - \frac{\gamma}{T} - \frac{C'}{T^4} p(1 + 2ap^{\frac{1}{2}}) + 0.1852cp + i_0, \quad (E)$$

in which

$$144\, Am(n+1) = C' \qquad \log C' = 10.79155,$$

and

$$144\, A = 0.1852 \qquad \log 144\, A = \bar{1}.26758.$$

84. Latent Heat.—Equation (C) gives the change of volume $v'' - v'$ when corresponding saturation values of p and T are sustituted in it. Having $v'' - v'$, the latent heat may be calculated from the Clapeyon relation

$$r = A(v'' - v')T \frac{dp}{dT}. \quad (1)$$

Let this equation be written in the form

$$r = Ap(v'' - v')\frac{T}{p}\frac{dp}{dT}. \quad (2)$$

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The product $Ap(v'' - v')$ is the external latent heat ψ, therefore

$$r = \psi \frac{T}{p} \frac{dp}{dT}. \qquad (F)$$

Equation (B) gives an expression for $\frac{T}{p} \frac{dp}{dT}$.

Having r and ψ, the internal latent heat is found by taking their difference; thus

$$\rho = r - \psi. \qquad (3)$$

Also the thermal potential of the liquid is given by the difference of i'' and r; thus

$$i' = i'' - r. \qquad (4)$$

85. Energy of Steam.—The energy u of superheated steam is readily found from the defining equation

$$i = u + Apv.$$

Taking the pressure in pounds per square inch, we have

$$\begin{aligned} u &= i - 144Apv \\ &= i - 0.1852pv. \end{aligned} \qquad (1)$$

For saturated steam we have similarly

$$u'' = i'' - 0.1852\, pv''. \qquad (2)$$

86. Entropy of Steam.—Taking the general equation (II), Art. 67, and dividing both members by T, the result is the equation

$$ds = \frac{dq}{T} = c_p \frac{dT}{T} - A\left(\frac{\partial v}{\partial T}\right)_p dp. \qquad (1)$$

From the characteristic equation (C) we have

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{B}{p} + \frac{mn}{T^{n+1}}(1 + 3ap^{\frac{1}{3}}). \qquad (2)$$

Introducing this expression and the expression for c_p given by (D) in (1), we have

$$ds = \left[\frac{\alpha}{T} + \beta + \frac{\gamma}{T^2} + \frac{Amn(n+1)}{T^{n+2}} p(1 + 2ap^{\frac{1}{3}})\right]dT - \frac{AB}{p}dp - \frac{Amn}{T^{n+1}}(1 + 3ap^{\frac{1}{3}})dp. \qquad (3)$$

The integration of this exact equation gives the following expression for the entropy:

$$s = \alpha \log_e T + \beta T - \frac{1}{2}\frac{\gamma}{T^2} - AB \log_e p - \frac{Amn}{T^{n+1}} p(1 + 2ap^{\frac{1}{3}}) + s_0. \qquad (G)$$

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By applying the equation to the condition of saturated steam at 212° the constant of integration is found to be $s_0 = -0.08053$.

As in the case of equation (E), the factor 144 must be introduced in some of the terms if pressures are taken in pounds per square inch. If we take

$$144\,AB = C'' \qquad \log C'' = \bar{1}.04206,$$
$$144\,Amn = C''' \qquad \log C''' = 10.69464,$$

the equation may be written

$$s = \alpha \log_e T + \beta T - \frac{1}{2}\frac{\gamma}{T^2} - C'' \log_e p - \frac{C'''}{T^5}\, p(1 + 2ap^{\frac{1}{2}}) + s_0. \quad (G')$$

This equation gives S'', the entropy of saturated steam when corresponding saturation values of p and T are substituted in it. Having s'', the entropy of the water is obtained from the relation

$$s' = s'' - \frac{r}{T}. \quad (4)$$

87. Illustrative Example.—The following example shows in detail the steps in the computations of tabular values. It should be observed that the labor of computation is greatly abridged by a judicious arrangement of the work and by making use of values which appear several times.

Required the various properties of saturated steam at a temperature of 300° F.

$t = 300$ $\qquad$ $\log T = 2.8805850$
$T = 759.6$ $\qquad$ $\log T^2 = 5.7611700$
$\qquad\qquad\qquad\quad \log T^4 = 11.5223400$
$\qquad\qquad\qquad\quad \log T^5 = 14.4029250$

(a) First calculate the pressure p from formula (A), taking the individual terms as follows:

B/T	$C \log T$
$\log B = \bar{3}.6881209$	$\log T = 2.8805850$
$\log T = 2.8805850$	$0.0155 \log T = 0.044649$
$\log B/T = 0.8075359$	
$B/T = 6.420013$	

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DT		ET^2	
$\log D$	$= \bar{3}.6088020$	$\log E$	$= \bar{6}.1463$
$\log T$	$= 2.8805850$	$\log T^2$	$= 5.76117$
$\log DT$	$= 0.4893870$	$\log ET^2$	$= \bar{1}.90747$
DT	$= 3.085937$	ET^2	$= 0.808109$

$$\Delta = 0.00002\,[10 - 10 \times 0.7^2 + 0.7^4]$$
$$= 0.0001068$$

Add positive and negative terms separately and take the difference.

+		−	
A	$= 10.568808$	B/T	$= 6.420013$
ET^2	$= 0.808109$	$C \log T$	$= 0.044649$
	11.376917	DT	$= 3.085937$
	9.550706	Δ	$= 0.000107$
$\log p$	$= 1.826211$		9.550706

$p = 67.02$ lb. per sq. in.

(*b*) It is convenient now to calculate $\frac{T}{p}\frac{dp}{dT}$, which appears in the formula for the latent heat r. All the terms are known except $T\frac{d\Delta}{dt}$.

$$\frac{d\Delta}{dt} = 0.00002\left[-\frac{20}{100}\left(\frac{t-370}{100}\right) + \frac{4}{100}\left(\frac{t-370}{100}\right)^3\right]$$
$$= 0.00002\ (0.14 - 0.01372) = 0.000002526$$

$$\log \frac{d\Delta}{dt} = \bar{6}.40236$$
$$\log T = 2.88058$$
$$\log T\frac{d\Delta}{dt} = \bar{3}.28294 \qquad T\frac{d\Delta}{dt} = 0.001918$$

+		−	
B/T	$= 6.420013$	DT	$= 3.085937$
$2ET^2$	$= 1.616218$	$T\frac{d\Delta}{dt}$	$= 0.001918$
	8.036231		3.087855
	3.087855		
	4.948376	$= \left[\frac{B}{T} - DT + 2ET^2 - T\frac{d\Delta}{dt}\right]$	

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$$\begin{aligned} \log [\quad] &= 0.6944626 \\ \log 2.3026 &= 0.3622157 \\ & \quad 1.0566783 \\ 2.3026 [\quad] &= 11.39406 \\ D &= 0.0155 \\ \frac{T}{p}\frac{dp}{dT} &= 11.37856 \end{aligned}$$

(*c*) Next in order is the volume v''.

$\frac{BT}{p}$

$$\begin{aligned} \log B &= \bar{1}.774480 \\ \log T &= 2.880585 \\ \log \frac{1}{p} &= \bar{2}.173789 \\ \log \frac{BT}{P} &= 0.828854 \\ \frac{BT}{p} &= 6.7430 \\ & \quad 0.2851 \\ v'' - c &= 6.4579 \\ c &= 0.0175 \\ v'' &= 6.4754 \end{aligned}$$

$(1 + 3ap^{\frac{1}{4}})\frac{m}{T^4}$

$$\begin{aligned} \log p^{\frac{1}{4}} &= 0.91311 \\ \log 3a &= \bar{2}.71000 \\ \log 3ap^{\frac{1}{4}} &= \bar{1}.62311 \\ 1 + 3ap^{\frac{1}{4}} &= 1.4199 \\ \log (1 + 3ap^{\frac{1}{4}}) &= 0.15226 \\ \log m &= 10.825 \\ & \quad 10.97726 \\ \log T^4 &= 11.52234 \\ & \quad \bar{1}.45492 \\ (1 + 3ap^{\frac{1}{4}})\frac{m}{T^4} &= 0.2851 \end{aligned}$$

(*d*) The external latent heat $\psi = 144\, Ap(v'' - v')$ may now be found. $v'' - v' = v'' - c = 6.4579$.

$$\begin{aligned} \log 144\, A &= \bar{1}.26758 \\ \log p &= 1.82621 \\ \log (v'' - v') &= .81009 \\ \log \psi &= 1.90388 \\ \psi &= 80.15 \end{aligned}$$

(*e*) The latent heat r is the product of ψ and $\frac{T}{p}\frac{dp}{dT}$.

$$\begin{aligned} \log \psi &= 1.90388 \\ \log \frac{T}{p}\frac{dp}{dT} &= 1.05609 \\ \log r &= 2.95997 \\ r &= 911.95 \end{aligned}$$

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(*f*) The internal latent heat ρ is $r - \psi = 911.95 - 80.15 = 831.8$.

(*g*) The thermal potential i'' may now be computed from formula (*E*).

αT

$$\log \alpha = 1.50515$$
$$\log T = 2.88058$$
$$\log \alpha T = 4.38573$$
$$\alpha T = 243.07$$

$\frac{1}{2}\beta T^2$

$$\log \tfrac{1}{2}\beta = \bar{5}.79934$$
$$\log T^2 = 5.76117$$
$$\log \tfrac{1}{2}\beta T^2 = 1.56051$$
$$\tfrac{1}{2}\beta T^2 = 36.35$$

γ/T

$$\log \gamma = 4.37260$$
$$\log T = 2.88058$$
$$\log \gamma/T = 1.49202$$
$$\frac{\gamma}{T} = 31.05$$

$144\,Acp$

$$\log 144A = \bar{1}.26758$$
$$\log c = \bar{2}.24304$$
$$\log p = 1.82621$$
$$\log 144\,Acp = \bar{1}.33683$$
$$144\,Acp = 0.22$$

$\frac{C'}{T^4} p(1 + 2ap^{\frac{1}{2}})(= \kappa)$

$$\log p^{\frac{1}{2}} = 0.91311$$
$$\log 2a = \bar{2}.53391$$
$$\log 2ap^{\frac{1}{2}} = \bar{1}.44702$$
$$1 + 2ap^{\frac{1}{2}} = 1.2799$$
$$\log (1 + 2ap^{\frac{1}{2}}) = 0.10717$$
$$\log p = 1.82621$$
$$\log C' = 10.79155$$
$$12.72493$$
$$\log T^4 = 11.52232$$
$$\log \kappa = 1.20261$$
$$\kappa = 15.94$$

+		−	
$\alpha T =$	243.07	$\frac{\gamma}{T} =$	31.05
$\frac{1}{2}\beta T^2 =$	36.35	$\kappa =$	15.94
$144\,Acp =$	0.22		46.99
$i_0 =$	948.54		
	1228.18		
	46.99		
$i'' =$	1181.19		

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(*h*) $i' = i'' - r = 1181.19 - 911.95 = 269.24.$

(*i*) $u'' = i'' - 144Apv''$

$$\begin{aligned} \log 144A &= \bar{1}.26758 \\ \log p &= 1.82621 \\ \log v'' &= .81126 \\ & \quad 1.90505 \\ 144\,Apv'' &= 80.36 \\ u'' = 1181.19 - 80.36 &= 1100.83 \end{aligned}$$

(*j*) Finally the entropies are computed; for s'' the individual terms of formula (9) are

$\alpha \log_e T$

$$\begin{aligned} \log T &= 2.880585 \\ \log (\log T) &= 0.45948 \\ \log 2.3026 &= 0.36222 \\ \log (\log_e T) &= \overline{0.82170} \\ \log \alpha &= \bar{1}.50515 \\ \log (\alpha \log_e T) &= .32685 \\ \alpha \log_e T &= 2.12250 \end{aligned}$$

βT

$$\begin{aligned} \log \beta &= \bar{4}.10037 \\ \log T &= 2.88058 \\ \log \beta T &= \bar{2}.98095 \\ \beta T &= 0.09571 \end{aligned}$$

$144\,AB \log_e p$

$$\begin{aligned} \log p &= 1.82621 \\ \log (\log p) &= 0.26155 \\ \log 2.3026 &= 0.36222 \\ \log (\log_e p) &= \overline{0.62377} \\ \log 144A &= \bar{1}.26758 \\ \log B &= \bar{1}.77448 \\ \log 144\,AB \log_e p &= \bar{1}.66583 \\ 144\,AB \log_e p &= 0.46327 \end{aligned}$$

$\frac{1}{2}\frac{\gamma}{T^2}$

$$\begin{aligned} \log \tfrac{1}{2} &= \bar{1}.69897 \\ \log \gamma &= 4.37260 \\ & \quad 4.07157 \\ \log T^2 &= 5.76117 \\ \log \tfrac{1}{2}\gamma/T^2 &= \bar{2}.31040 \\ \frac{1}{2}\frac{\gamma}{T^2} &= 0.02044 \end{aligned}$$

$144\frac{Amn}{T^6}p(1 + 2ap^{\frac{1}{2}})(= P)$

$$\begin{aligned} \log 144\,Amn &= 10.69464 \\ \log p &= 1.82621 \\ \log (1 + 2ap^{\frac{1}{2}}) &= 0.10717 \\ & \quad 12.62802 \\ \log T & \quad 14.40292 \\ \log P &= \bar{2}.22510 \\ P &= 0.01679 \end{aligned}$$

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+		−	
$\alpha \log_e T$	= 2.12250	$144\,AB \log_e p$	= 0.46327
βT	= 0.09571	$\frac{1}{2}\gamma/T^2$	= 0.02044
	2.21821	P	= 0.01679
	0.58103	s_0	= 0.08053
s''	= 1.63718		0.58103

$$\log r = 2.95997$$
$$\log T = 2.88058$$
$$\log r/T = 0.07939$$
$$\frac{r}{T} = 1.2006$$

$$s' = s'' - \frac{r}{T} = 1.63718 - 1.2006 = 0.43658.$$

Properties of the Fluids used in Refrigeration

88. Properties of Ammonia.—Probably the most accurate formulation of the properties of ammonia, on the basis of existing experimental data, is that accomplished by Mosher. The results of Mosher's work are embodied in the author's "Properties of Steam and Ammonia." The U. S. Bureau of Standards has undertaken comprehensive experiments on the various properties of this fluid and has already published some of the results obtained. With the completion of this work new tables may be expected, which in accuracy will compare with the tables of the properties of water vapor. Until the new tables appear Mosher's tables may be used with confidence.

The pressure and temperatures of saturated ammonia vapor are connected with those of saturated steam by the following equation. At the *same* pressure let T_w and T_a denote, respectively, the absolute temperature of steam and of ammonia; then

$$\frac{1}{T_a} = 1.70343\,\frac{1}{T_w} - 0.0002242. \qquad (1)$$

For the specific volume v' of liquid ammonia between −60° and 160° F., Mosher gives the equation

$$v' = 0.06335 - 0.016 \log (273.2 - t), \qquad (2)$$

and for the latent heat r, he gives

$$\log r = 1.856064 + 0.37 \log (273.2 - t). \qquad (3)$$

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The characteristic equation of superheated ammonia is

$$v + 0.10 = 0.6321\frac{T}{p} - \frac{m}{T^5}, \quad (\log m = 12.90000) \qquad (4)$$

with p in pounds per square inch. From this equation the following equations for c_p, i, and s are deduced.

$$c_p = 0.382 + 0.000174T + \frac{C'p}{T^6}. \quad (\log C' = 13.64471). \qquad (5)$$

$$i = 0.382T + 0.000087T^2 - \frac{C''p}{T^5} - 0.0185p + 358. \qquad (\log C'' = 12.94573) \qquad (6)$$

$$s = 0.8796 \log T + 0.000174T - 0.2795 \log p - \frac{C'''p}{T^6} - 0.8266. \qquad (\log C''' = 12.86655) \qquad (7)$$

In these formulas p is to be taken in pounds per square inch.

By means of the preceding formulas all the properties of saturated and superheated ammonia may be calculated.

89. Properties of Sulphur Dioxide.—The properties of the saturated vapor of SO_2 are mainly based on the researches of Cailletet and Mathias. Some of these properties are given by the following empirical formulas.

$$v' = 0.0113, \qquad (1)$$

$$c' = 0.3194 + 0.00065(t - 32), \qquad (2)$$

$$s' = 0.00065 \log_e \frac{T}{491.6} = 0.00065(t - 32) \text{ approx.} \qquad (3)$$

$$\frac{r}{T} = 0.3327 - 0.00129(t - 32).$$

90. Properties of Carbon Dioxide.—The following formulas due to Mollier represent the experiments of Amagat.

$T_k = 547.83°$ F., the critical temperature of CO_2 on the absolute scale.

$$p = 42.2056\left(\frac{T}{180} - 1\right)^{4.525}, \qquad (1)$$

$$r = 0.6816\, T^{0.43}(T_k - T)^{0.43}, \qquad (2)$$

$$c' = 0.000185T + 0.285\frac{r}{T} + 0.215\frac{r}{T_k - T}, \qquad (3)$$

$$s' = 0.10155 + 0.000185(t - 32) - \frac{r}{2T}. \qquad (4)$$

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Tables of the properties of saturated vapor of SO_2 and CO_2 are given in the Mechanical Engineers Handbook (L. S. Marks editor), pp. 336,337. The properties of the superheated vapor are not sufficiently well known to justify tabulation.

EXERCISES

1. For some assumed temperature of saturated steam calculate all the properties given in the steam table.

2. Calculate the values of i, s, and v for superheated steam having the following condition.

(*a*) p = 20 lb. per sq. in. t = 310° F.
(*b*) p = 190 lb. per sq. in. t = 540° F.
(*c*) p = 78 lb. per sq. in. t = 470° F.

3. Calculate values of $\psi = Ap(v'' - v')$ for several pressures and verify the results by the difference $r - \rho$ taken from the steam tables.

4. Calculate the saturation temperature of ammonia for the following pressures: (*a*) 40 lb.; (*b*) 160 lb. per sq. in.

5. Having the temperatures, find for these pressures the latent heat r and the saturation volume v''. Check results with the table of properties of ammonia.

6. If CO_2 vapor is condensed at a temperature of 68° F. to what pressure must it be compressed?

7. Calculate the latent heat r of CO_2 at a temperature of 88.23° F. Interpret the result.

8. At the same temperature, 70° F., compare the latent heats of ammonia sulphur dioxide, and carbon dioxide.

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CHAPTER VIII

CHANGES OF STATE OF VAPOR MEDIA

91. Liquid and Saturation Curves.—If for various temperatures the corresponding values of s', the entropy of the liquid, be laid off as abscissæ, the result is a curve s', Fig. 23. This is called the **liquid** curve. If, likewise, values of

$$s'' = s' + \frac{r}{T}$$

be laid off as abscissæ, a second curve s'' is obtained. This is called the **saturation** curve.

The form of the saturation curve has an important relation to the behavior of a saturated vapor. For nearly all vapors, the curve has the general form shown in Fig. 23; that is, the entropy s'' decreases with rising temperature. In the case of ether vapor, however, the entropy increases with rising temperature and the curve has, therefore, the same general direction as the liquid curve s'

92. Critical States.—The region between, the limit curves v', v'' (Fig. 21) or s', s'' (Fig. 23) is the region of mixtures of saturated vapor and liquid. The fact that these two curves approach each other as the temperature is increased suggests that a temperature may be reached above which it is impossible for a mixture of liquid and vapor to exist. Let it be assumed that the two limit curves merge into each other at the point H (Fig. 25), and thus constitute a single curve, of which the liquid and saturation curves, as we have previously called them, are merely two branches. The significance of this assumption may be gathered from the following considerations.

Let superheated vapor in the initial state represented by point A (Fig. 25 and 26) be compressed isothermally. Under usual conditions, the pressure will rise until it reaches the pressure of saturated vapor corresponding to the given constant tempera-

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ture t, and the state of the vapor will then be represented by point B on the saturation curve. Further compression at constant temperature results in condensation of the saturated vapor, as indicated by the line BC. If the liquid be compressed isothermally, the volume will be decreased slightly as the pressure rises, and the process will be represented by curve CD. The isothermal has therefore three distinct parts: along AB the fluid is superheated vapor, along BC a mixture, and along CD a liquid. If the initial temperature be taken at a higher value t', the result will be similar except that the segment $B'C'$ will be

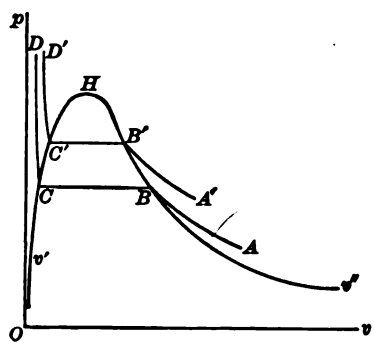


Fig. 25.

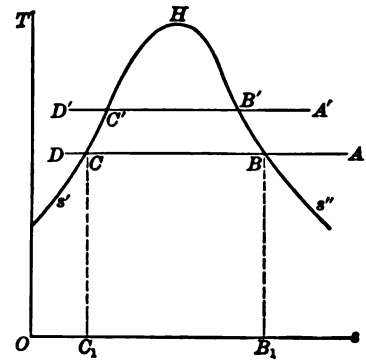


Fig. 26.

shorter. If the limit curves meet at point H, it is evident that the temperature may be chosen so high that this horizontal segment of the isothermal disappears; in other words, the isothermal lies entirely outside of the single limit curve.

In Fig. 25 the segment BC represents the difference $v'' - v'$ between the volume v'' of saturated vapor and the volume v' of the liquid; and in Fig. 26, the area B_1BCC_1 represents the latent heat r of vaporization. For the isothermal t_k that passes through H, the segment BC reduces to zero; hence, for this temperature we have

$$v'' - v' = 0, \text{ or } v'' = v',$$

and

$$r = 0.$$

The second result also follows from the first when we consider the Clapeyron equation

$$r = AT(v'' - v')\frac{dp}{dT}.$$

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The experiments of Andrews show that the condition just described may be actually attained. The isothermals for carbon dioxide as determined by Andrews are shown in Fig. 27. For $t = 13.1°$ and 21.5°C. the horizontal segments corresponding to condensation are clearly marked. For $t = 31.1°$ the horizontal segment disappears and there is merely a point of inflexion in the curve. At 48.1° the point of inflexion disappeared, and the isothermal has the general form of the isothermal for a perfect gas.

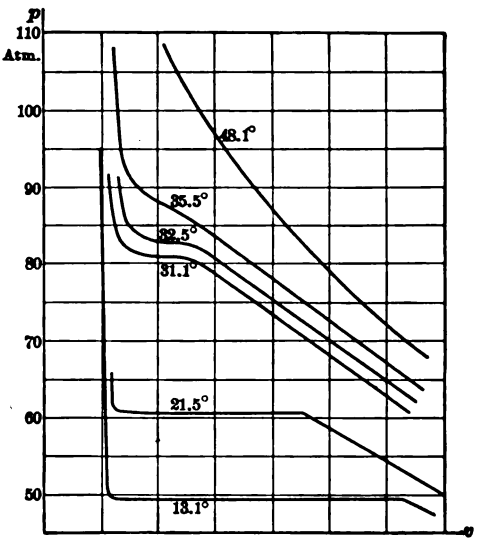


FIG. 27.

The temperature t_k was called by Andrews the **critical temperature.** It has a definite value for any liquid. The pressure p_k and volume v_k indicated by the point H are called respectively the critical pressure and critical volume. Values of t_k and p_k for various substances are given in the following table:

Substance	t_k, degrees C.	p_k, atmospheres
Water	374.5	217.7
Ammonia	130.0	115.0
Ether	197.0	35.77
Sulphur dioxide	155.4	78.9
Carbon dioxide	30.92	77.0
Carbon disulphide	277.7	78.1
Nitrogen	−146.0	35.0
Oxygen	−118.0	50.0
Hydrogen	−220.0	20.0
Air	−140.0	30.0

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It appears from the definition of the critical temperature that it is possible for a mixture of liquid and vapor to exist only for temperatures below t_k. At higher temperatures the mass remains homogeneous throughout the entire range of pressure. Although at sufficiently high pressure the fluid may be in the liquid state, the closest observation fails to show where the gaseous state ceases and the liquid state begins. As stated by Andrews, the gaseous and liquid states are to be regarded as widely separated forms of the same state of aggregation.

It will be observed that the permanent gases, air, nitrogen, etc. have critical temperatures that are far below the zero of the C. or F. scale The liquefaction of one of these gases requires a reduction of temperature to some point below the critical temperature; thus for the production of liquid air a temperature below −140°C. (−220° F.) is necessary.

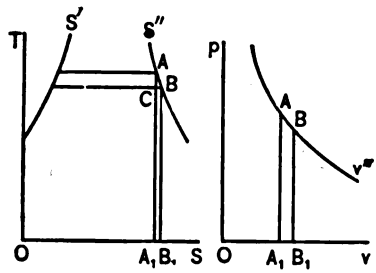


FIG. 28.

93. Specific Heat of a Saturated Vapor.—A change of state of considerable theoretical interest is that in which a vapor expands, or is compressed, while remaining in the saturated condition. Such a change is represented by a movement of the statepoint on the saturation curve s''. Consider, for example, the change indicated by BA, Fig. 28. This represents a rise of temperature of the saturated vapor during which the vapor remains in the saturated condition. The process must evidently be accompanied by the withdrawal of heat represented by the area B_1BAA_1; and the reverse process, fall in temperature from A to B, is accompanied by the addition of heat represented by the same area. It appears, therefore, that along the saturation curve the ratio $\frac{\Delta q}{\Delta t}$ is negative (except in the case of ether); that is, the specific heat of a saturated vapor is, in general, negative.

An explanation of this behavior of saturated vapor is found in a comparison of the change of energy and external work done. Let points A and B, for example, represent, respectively, saturated steam at pressures of 105 lb. and 95 lb. per sq. in. From the steam table the volumes are respectively

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4.240 and 4.663 cu. ft. per pound. It may be assumed that for this small change the area A_1ABB_1 on the pv-plane is a trapezoid; hence the external work done by the steam is

$$144 \times \frac{105 + 95}{2} (4.663 - 4.240) = 6091 \text{ ft.-lb.} = 7.83 \text{ B. t. u.}$$

The intrinsic energy of saturated steam at 105 lb. is 1106.8 B. t. u., that at 95 lb. is 1105.5 B. t. u. Consequently, in expanding from A to B, the steam gives up 1.3 B. t. u. of its energy, and the deficit, 6.53 B. t. u., must be supplied from external sources. If the heat is not supplied from outside, that is, if the expansion is adiabatic, as shown by AC, some of the steam condenses and gives up by condensation the heat required. It follows that saturated steam must partly condense when it expands adiabatically.

The specific heat c'' of the saturated vapor for a change of state along the saturation curve has, as we have seen, a negative value. An expression for this specific heat may be obtained as follows. The entropy of the saturated vapor is given by the equation

$$s'' = s' + \frac{r}{T}; \tag{1}$$

hence the change of entropy corresponding to a change of temperature is obtained by differentiating (1), thus

$$ds'' = ds' + d\left(\frac{r}{T}\right). \tag{2}$$

But
$$ds' = \frac{c'dT}{T}, \tag{3}$$

and similarly for the saturation curve,

$$ds'' = \frac{c''dT}{T}. \tag{4}$$

Substituting these values ds' and ds'' in (2), the result is

$$c'' = c' + T\frac{d}{dT}\left(\frac{r}{T}\right),$$

or
$$c'' = c' + \frac{dr}{dT} - \frac{r}{T}. \tag{5}$$

94. Constant Quality Curves.—Any point between the curves s' and s'', Fig. 29, represents a mixture of liquid and vapor, the ratio x depending upon the position of the point. It is possible, therefore, to draw between the curves s' and s'' a series of constant-x lines. Each of the horizontal segments $A'A''$, $B'B''$, etc., is divided into a convenient number (say 10) of equal parts

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and corresponding points are joined by curves. The successive curves, therefore, are the loci of points for which $x = 0.1$, $x = 0.2$, etc. For the liquid curve $x = 0$, for the saturation curve $x = 1$.

The equation of one of the curves is

$$s = s' + x\frac{r}{T}, \tag{1}$$

in which x is constant.

If the state point follows one of the constant-x curves near the saturation curve, that is, if the mixture expands maintaining a constant quality, as $x = 0.8$, heat must be added, as in the case of vapor remaining saturated. If, however, x is small, as 0.1 or 0.2, the expansion is accompanied with a loss of heat. At a given pressure there is some value of x at which an indefinitely small expansion with x constant is also adiabatic. In other words, at this point the constant-x curve has a vertical tangent. The condition required is evidently

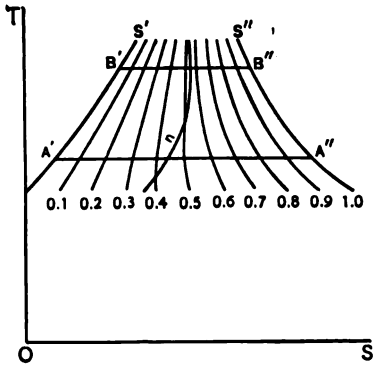


FIG. 29.

$$dx = 0 \quad \text{when } ds = 0.$$

From equation (1) we have at such a point

$$0 = ds = ds' + x\,d\left(\frac{r}{T}\right)$$

or

$$x = -\frac{ds'}{d\left(\frac{r}{T}\right)}.$$

For the differentials of s' and r/T the tabular differences for a temperature difference of one degree may be substituted. Thus for the following temperatures we have

$t =$	100°	200°	300°	400°
$\Delta s' =$	0.00175	0.0015	0.00135	0.0012
$\Delta\frac{r}{T} =$	−0.0043	−0.0032	−0.0026	−0.00225
$x =$	0.407	0.469	0.520	0.523

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The locus of the points thus determined is the curve n, Fig. 29; it is sometimes called the **zero curve.**

95. Variation of Quality in Adiabatic Changes.—Let the point B, Fig. 30, represent the state of saturated vapor. Adiabatic expansion is represented by a vertical line BE, the final point E being at lower temperature; adiabatic compression is shown by a vertical line BG. With a saturation curve of the form shown, it appears that during adiabatic expansion some of the vapor condenses, while adiabatic compression results in superheating. If the state point is originally at N, so that x is somewhat less than 1 (say 0.7 or 0.8), then adiabatic expansion is accompanied by a decrease in x, adiabatic compression by an increase of x.

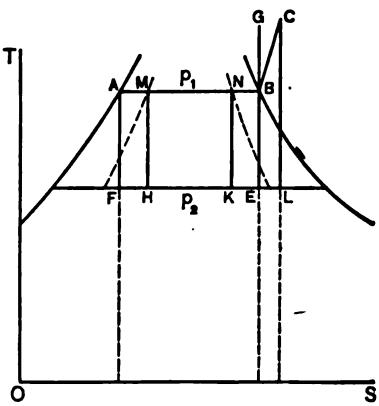


FIG. 30.

If the saturation curve slopes in the other direction, as in the case of ether, the conditions just stated will, of course, be reversed.

Adiabatic expansion of the liquid is represented by the line AF; evidently some of the liquid is vaporized during the process. If the mixture is originally mostly liquid, as indicated by a point M near the curve s', then adiabatic expansion results in an increase of x, adiabatic compression in a decrease of x.

In general, adiabatic expansion is accompanied by condensation, or decrease of quality when the state point lies between the zero curve and the saturation curve.

96. Adiabatic Expansion.—Let a mixture of liquid and vapor, having initially the pressure p_1 and quality x_1, expand adiabatically to the lower pressure p_2. In the initial state represented by point N, Fig. 30, the entropy of unit weight is

$$s_1 = s'_1 + \frac{x_1 r_1}{T_1},$$

and in the final state represented by point K the entropy is

$$s_2 = s'_2 + \frac{x_2 r_2}{T_2}.$$

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Therefore, since $s_1 = s_2$,

$$s'_1 + \frac{x_1 r_1}{T_1} = s'_2 + x_2 \frac{r_2}{T_2}. \tag{1}$$

Values of s' and $\frac{r}{T}$ for the known pressures p_1 and p_2 are given in the tables of the properties of the vapor; hence x_2 is the only unknown quantity.

If in the initial state only liquid is present, as indicated by point A, then $x_1 = 0$, and the quality at the final state F is given by the equation

$$s'_1 = s'_2 + x_2 \frac{r_2}{T_2}. \tag{2}$$

If the vapor is initially superheated, as indicated by point C, the quality in the final state L is determined from the relation

$$s_c = s'_2 + x_2 \frac{r_2}{T_2}. \tag{3}$$

The value of the initial entropy s_c is given in the table of properties of the superheated vapor.

The volume of one pound of the mixture in the final state (pressure p_2, quality x_2) is

$$v = x_2(v''_2 - v') + v' \tag{4}$$

or approximately

$$v = x_2 v''_2. \tag{5}$$

The external work done is, as in all adiabatic cases, the decrease of energy of the fluid; hence if u_1 and u_2 denote, respectively, the energy per pound in B. t. u. at the initial and final states,

$${}_1W_2 = JM(u_1 - u_2) \tag{6}$$

If the final state is that of a mixture, as is nearly always the case, the energy u_2 is given by the expression

$$u_2 = u''_2 - (1 - x)\rho_2. \tag{7}$$

Similarly, if the fluid is a mixture in the initial state (as at point C)

$$u_1 = u''_1 - (1 - x)\rho_1; \tag{8}$$

but if it is in the state of superheated vapor (as shown by point D) the initial energy is most easily determined from the equation

$$u_1 = i_1 - 0.1852\, p_1 v_1. \tag{9}$$

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EXAMPLE. Let the initial pressure p_1 of steam be 150 lb. per sq. in. and the pressure after expansion $p_2 = 16$ lb. per sq. in. Required the final quality, the final volume per pound, and the external work per pound (*a*) when the initial quality is $x_1 = 0.96$; (*b*) when the steam is initially superheated to 520° F.; (*c*) when the fluid is initially water, that is, $x_1 = 0$.

For the three cases the initial entropies are, respectively:

(*a*) $s''_1 - (1 - x_1)\frac{r_1}{T_1} = 1.5704 - 0.03 \times 1.0573 = 1.5387$;

(*b*) $s_1 = 1.6708$ from the properties of superheated steam.

(*c*) $s'_1 = 0.5131$.

Therefore we have the following equations from which to determine x_2.

(*a*) $1.5387 = s_2' + x_2\frac{r_2}{T_2} = 0.3184 + 1.4337x_2$; $x_2 = 0.851$.

(*b*) $1.6708 = 0.3184 + 1.4337x_2$; $x_2 = 0.943$.

(*c*) $0.5131 = 0.3184 + 1.4337x_2$; $x_2 = 0.136$.

The specific volume at $p_2 = 16$ lb. is 24.76 cu. ft. per lb. Hence the final volumes are:

(*a*) $v_2 = 0.851 \times 24.76 = 21.08$ cu. ft.

(*b*) $v_2 = 0.943 \times 24.76 = 23.36$ cu. ft.

(*c*) $v_2 = 0.136 \times 24.76 = 3.36$ cu. ft.

The initial values of u_1, energy per pound are

(*a*) $u_1'' - (1 - x)\rho_1 = 1110.9 - 0.03 \times 781.6 = 1087.5$ B. t. u.

(*b*) $i_1 - 0.1852p_1v_1 = 1284.7 - 0.1852 \times 150 \times 3.78 = 1179.7$ B. t. u.

(*c*) $u_1'' - \rho_1 = 1110.9 - 781.6 = 329.3$ B. t. u.

The values of u_2 for the three cases are obtained from the equation $u_2 = u_2'' - (1 - x_2)\rho_2$ with $u_2'' = 1080.0$ and $\rho = 895.8$ B. t. u. for $p_2 = 16$ lb. Hence for (*a*) $u_2 = 946.5$; for (*b*) $u_2 = 1028.9$; for (*c*) $u_2 = 306.0$ B. t. u.

The external work in the first case is

(*a*) $W = J(1087.5 - 946.5) = 109600$ ft. lb.

and for the other cases

(*b*) $W = J(1179.7 - 1028.9) = 117200$ ft. lb.

(*c*) $W = J(329.3 - 306.0) = 18120$ ft. lb.

97. Constant Pressure Change of State.—In the first place, it is assumed that the fluid remains a mixture throughout the change, as indicated, for example, by the path *MN*, Fig. 30. In this case the change is also *isothermal*. Let the subscripts 1 and 2 refer, as usual, to the initial and final states; then

$$v_1 = x_1(v'' - v') + v', \qquad v_2 = x_2(v'' - v') + v',$$

and the change of volume is therefore

$$v_2 - v = (x_2 - x_1)(v'' - v') \tag{1}$$

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The external work is

$$ {}_1W_2 = p(v_2 - v_1) = p(x_2 - x_1)(v'' - v') $$
$$ = J\psi(x_2 - x_1). \qquad (2) $$

The change of energy in B. t. u. per pound is

$$ u_2 - u_1 = \rho(x_2 - x_1), \qquad (3) $$

and the heat absorbed is

$$ {}_1q_2 = i_2 - i_1 = r(x_2 - x_1). \qquad (4) $$

Secondly, let the initial state be that of a mixture, as indicated by point N, Fig. 30, and the second state that of superheated vapor as indicated by the point C. With the pressure p and quality x_1 in the initial state known, v_1, u_1, and i_1 may be calculated as previously explained. For the final state, v_2 and i_2 may be found in the table of properties of superheated steam and u_2 may be determined from the relation $u_2 = i_2 - 0.1852pv_2$. The heat absorbed is

$$ {}_1q_2 = i_2 - i_1 = i_2 - i'' + (1 - x)r, \qquad (5) $$

and the work done is

$$ {}_1W_2 = p(v_2 - v_1) \qquad (6) $$

EXAMPLE. Steam in a boiler has a pressure of 180 lb. and quality $x = 0.985$. It leaves the superheater at a temperature of 540° F.

In this case, $i_1 = 1197.2 - 0.015 \times 852 = 1184.4$ B. t. u., and i_2 from the table is 1292.1. The heat absorbed per pound of steam passing through the superheater is therefore $1292.1 - 1184.4 = 107.7$ B. t. u.

Also $v_2 = 3.21$, $v_1 = 0.985 \times 2.536 = 2.498$; hence the work done by the steam in expanding is $144 \times 180(3.21 - 2.498) = 18400$ ft. lb.

98. Constant Volume Change of State.—Let a mixture of quality x_1 and pressure p_1 be cooled at constant volume to a final temperature t_2 corresponding to the pressure p_2. The final quality x_2 and the heat rejected are required. Since the volumes v_1 and v_2 are equal, we have

$$ x_1(v_1'' - v_1') + v_1' = x_2(v_2'' - v_2') + v_2'. \qquad (1) $$

The simpler approximate relation

$$ x_1v_1'' = x_2v_2'' \qquad (2) $$

is, however, sufficiently accurate. In this equation v_1'' and v_2'' are the known saturation volumes corresponding to the pressures p_1 and p_2. The external work being zero, the heat abstracted

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per pound of mixture is equal to the decrease of intrinsic energy that is

$$-{}_1q_2 = u_1 - u_2, \tag{3}$$

in which

$$u_1 = u_1'' - (1 - x)\rho_1,$$
$$u_2 = u_2'' - (1 - x)\rho_2$$

99. Curves on the Ts-plane.—The families of curves that represent the various changes of state may be drawn on the Ts-plane, as shown in Fig. 31; the chart thus constructed is useful in showing the variation of the various properties as the fluid undergoes the prescribed change.

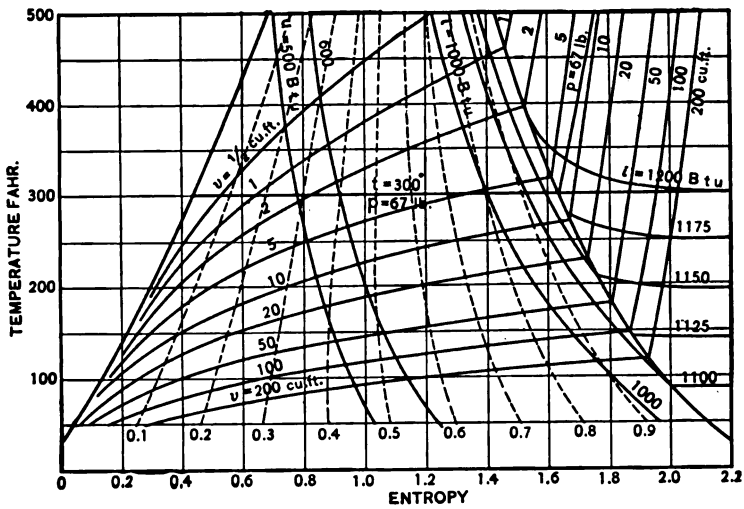


FIG. 31.

The liquid and saturation curves are plotted from the data furnished by the tables of the properties of the vapor, and the constant quality lines are drawn as explained in Art. 94. Between the liquid and saturation curves horizontal lines are lines of constant temperature and also of constant pressure; thus in the case of steam, the same line represents $t = 300°$ F. and $p =$ 67 lb. per sq. in. In the region of superheat, however, the line $t = 300°$ continues horizontal but the line $p = 67$ lb. per sq. in. rises sharply from the saturation curve.

The constant volume curves, within the region of mixtures, are

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determined as follows. The expression for the volume of a mixture is

$$v_m = x(v'' - v') + v', \tag{1}$$

from which we have

$$x = \frac{v_m - v'}{v'' - v'}. \tag{2}$$

For chosen temperatures t_1, t_2, t_3, etc. the saturation volumes, v''_1, v''_2, v''_3, etc. are known, and from (2) the corresponding values of x are found. The value of x_1 locates a definite point on the t_1 line, that of x_2 a point on the t_2 line, and so on. The locus of these points is a curve any point of which represents a mixture having the given volume v_m. In the region of superheat the constant volume lines are plotted from the tables of the properties of the superheated vapor. It will be observed that the constant volume lines show a sharp break at the saturation curve, and in the superheat region they are nearly straight lines slightly inclined to the vertical. Note also that in the superheat region the constant volume lines are steeper than the constant pressure lines.

Lines of constant thermal potential are determined from the relation

$$i_m = i' + xr, \tag{3}$$

from which

$$x = \frac{i_m - i'}{r}. \tag{4}$$

In the figure the curves $i = 1000$, $i = 1100$, and $i = 1150$ B. t. u. have been drawn. The first line lies wholly in the mixture region, the second line intersects the saturation curve at $t = 90°$ F., at which temperature $i'' = 1100$ B. t. u., and the third line meets the saturation curve at $t = 207.5°$ F. In the superheat region the constant-i curve at first curves downward from the saturation curve and then approaches more and more a horizontal constant-temperature line. In the case of a perfect gas isothermal lines are also constant-i lines; hence as the state point representing the superheated vapor recedes from the saturation curve, that is as the vapor becomes more highly superheated, the condition of the perfect gas is approached.

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Lines of constant energy may be located by means of the relation

$$u_m = u'' - (1 - x)\rho, \tag{5}$$

whence

$$1 - x = \frac{u'' - u_m}{\rho} \tag{6}$$

The lines $u = 500$, and $u = 600$ B. t. u. are shown in the figure. The constant-u lines have the same general form as the constant-i lines but they are more nearly vertical.

From the general course of the groups of curves the behavior of the mixture (or superheated vapor) during a given change of state may be traced. For example: (1) If the saturated vapor expands adiabatically, v increases, p, t, u, and i decrease. (2) If a mixture is heated and kept at constant volume p, t, x, u, i, and s all increase.

100. The Mollier Chart.—The thermal potential i being a function of the state only may be used as a coordinate along with any other chosen variable. For vapors a graphic representation on a plane with i as the ordinate and the entropy s as the abscissa has many advantages. This scheme of representation was first conceived by Dr. R. Mollier of Dresden.

Fig. 32 shows a Mollier chart for steam, the data for which were taken from the "Properties of Steam and Ammonia." The saturation curve is determined by plotting corresponding values of i'' and s''. Above this curve is the region of superheat traversed by constant temperature lines running nearly horizontal; below the curve are the lines of constant quality $x = 0.98$, 0.96, etc. The constant pressure lines cross the constant quality lines and the saturation curve approximately at right angles.

The Mollier chart is useful in the solution of certain classes of problems, especially those that relate to the flow of vapors. The following examples illustrate some of the applications.

Ex. 1. Find the heat required to change one pound of a mixture of steam and water at a pressure of 150 lb. per sq. in. and quality 0.96 to superheated steam at the same pressure and a temperature of 550° F.

The process is conducted at constant pressure, therefore the heat added is the increase of potential i. From the chart $i_1 = 1160$ B. t. u. and $i_2 = 1300$ B. t. u.; hence $q = 1300 - 1160 = 140$ B. t. u.

Ex. 2. A mixture has initially a pressure of 200 lb. per sq. in. and quality 0.95. If the state changes according to the law $i = \text{const.}$ (which is the

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case when steam is wire-drawn), at what pressure will the steam become saturated?

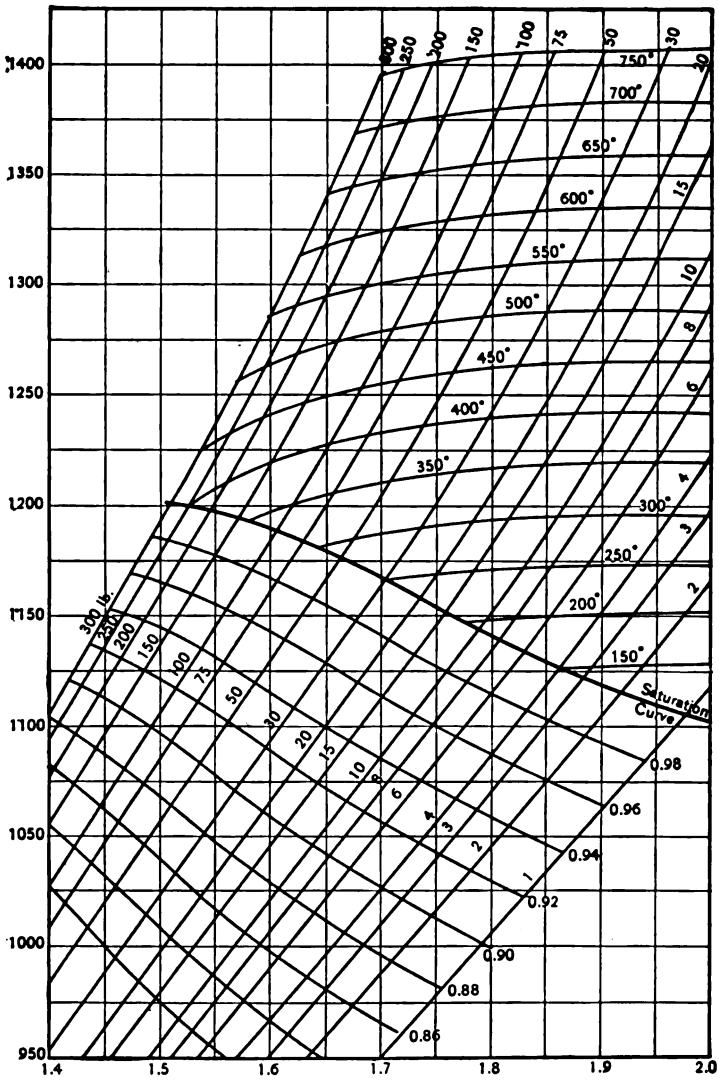


FIG. 32.

Through the point that represents the initial state we follow the constant-t (horizontal) line to the saturation curve and find the pressure to be 19 lb. per sq. in. approximately.

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Ex. 3. Steam at a pressure of 225 lb. per sq. in. and superheated to 550° F. expands adiabatically to a pressure of 2 lb. per sq. in. Required (*a*) the final quality; (*b*) the pressure at which the steam is just saturated.

Through the initial point follow the constant-s or vertical line to its intersection with the line $p = 2$. The quality indicated is 0.841. The intersection of the same line with the saturation curve indicates a pressure of about 68 lb. per sq. in.

EXERCISES

1. Determine the volume v, thermal potential i, energy u, and entropy s of one pound of steam (or mixture) for each of the following states:

	p	x	t
(*a*)	60 lb.	0.87	
(*b*)	135 lb.		460° F.
(*c*)	220 lb.		560° F.
(*d*)	95 lb.	0.11	

2. A mixture in state 1 absorbs heat at constant pressure until state 2 is attained. For each of the following cases find heat absorbed, change of energy, and external work per pound of fluid.

	State 1		State 2	
	p	x	x	t
(*a*)	72 lb.	0.94		440° F.
(*b*)	210 lb.	0.97		650° F.
(*c*)	130 lb.	0.72	1.00	
(*d*)	105 lb.	0.20	0.95	

3. One pound of saturated steam at 140 lb. pressure is superheated at constant pressure; also 1 lb. of saturated steam at 100 lb. pressure is superheated at constant volume. At what temperature will the final state in the two cases be the same? Find the heat absorbed in each of the two cases.

Ans. At 600° F. (*a*) 133.2 B. t. u.; (*b*) 105.2 B. t. u.

4. Find the external work and the change of energy for each of the changes of state in Ex. 3.

5. For saturated steam at 233 lb. pressure, $i = 1200$ B. t. u. Take a series of lower pressures, as 200, 150, 100, 50, 20 lb., etc., and keeping i at 1200, determine the superheat for the successive pressures. Plot a curve of superheat against pressure.

6. Let 1 lb. of steam (or mixture) in the initial state indicated expand adiabatically to the pressure p_2. Find x_2, v_2, and the external work in each case.

	State 1			State 2
	p_1	x_1	t	p_2
(*a*)	225 lb.		550	1.2 lb.
(*b*)	90 lb.	0.98		16 lb.
(*c*)	175 lb.	0.95		3 in. mercury
(*d*)	80 lb.	0.00		15 lb.

7. Let a mixture of steam and water at a pressure of 27 lb. per sq. in. with a quality $x = 0.93$ be compressed adiabatically. (*a*) At what pressure

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will it become saturated? (*b*) Find the external work per pound required for the compression.

8. Saturated ammonia at a temperature of 10° F. is compressed adiabatically to a pressure of 170 lb. per sq. in. (*a*) Find the values of t, i, and u for the final state. (*b*) Find the work of compression per pound.

9. If the ammonia is now cooled and condensed at the constant pressure 170 lb., how much heat is given up by one pound?

10. Water at a temperature of 185° F. is pumped into a boiler in which the pressure is 165 lb. per sq. in. How much heat per pound is required to convert the water into steam having a quality of 0.975?

11. If 4.2 lb. of a mixture of steam and water at a pressure of 120 lb. per sq. in. occupy a volume of 6 cu. ft., what is the quality? Upon the addition of heat the mixture expands at constant pressure until the water is evaporated. Find the heat added and the external work.

Ans. 2282 B. t. u.; 166,650 ft.-lb.

12. The initial state of a mixture of steam and water is $p_1 = 120$ lb. per sq. in., $x_1 = 0.95$. Let the pressure be reduced to 50 lb. per sq. in. by each of the following changes of state. (*a*) Adiabatic expansion; (*b*) expansion with i constant; (*c*) expansion with u constant; (*d*) cooling at constant volume. Find for each case the final quality x_2. For cases (*a*) and (*d*) find the external work and the heat absorbed or rejected per pound.

13. Plot on cross-section paper the four changes of state given in Ex. 12.

14. Taking the initial state given in Ex. 12, find the pressure at which the steam becomes saturated when the expansion follows the law i = constant. What happens if the expansion proceeds to a still lower pressure?

15. In a refrigerating machine ammonia enters the condenser coils at a pressure of 160 lb. per sq. in. and a temperature of 190° F. The ammonia is then cooled and condensed at this pressure. Find (*a*) the heat that must be removed to bring the ammonia to the saturation state; (*b*) the total heat removed in both cooling and condensation.

16. Liquid ammonia under a pressure of 160 lb. per sq. in. and at the corresponding saturation temperature passes through an expansion valve and its pressure is thus reduced to 45 lb. per sq. in. For this process $i_1 = i_2$. Determine the quality x_2 in the final state.

17. Referring to Ex. 15 and 16, the ammonia at 45 lb. pressure and having the quality x_2 absorbs heat from surrounding brine and is thus vaporized at constant pressure. Find the heat absorbed from the brine by 1 lb. of the fluid.

18. From the table for superheated steam find approximately the specific heat of superheated steam at various temperatures by taking $c_p = \Delta i / \Delta t$. In this way plot curves showing the variation of c_p with t for the following pressures: 20, 80, 140, 250 lb. per sq. in.

19. Saturated steam at 180 lb. per sq. in. is superheated at this pressure to a temperature of 580°. For one pound find the heat required, the change of energy, and change of entropy.

20. A vessel contains 24 cu. ft. of steam at 65 lb. per sq. in. pressure and a temperature of 370° F. Heat is absorbed from the steam until in the

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final state the quality is $x = 0.10$. Find the heat taken away (*a*) if the change proceeds under constant pressure; (*b*) if it proceeds at constant volume. Show the two changes of state by curves on the TS-plane.

21. Steam at a pressure of 80 lb. per square inch expands, remaining saturated, until the pressure drops to 50 lb. per square inch. Find approximately the heat that must be added to keep the steam in the saturated condition. Ans. 28.9 B. t. u. per pound

22. Water at a temperature of 352° F. and under the corresponding pressure expands adiabatically until the pressure drops to 30 lb. per square inch. Find the per cent. of water vaporized during the process. Find the work of expansion per pound of water.

23. Two vessels, one containing M_1 lb. of mixture of steam and water at a pressure p_1 and quality x_1, the other M_2 lb. at a pressure p_2 and quality x_2, are placed in communication. No heat enters or leaves while the contents of the vessels are mixing. Derive equations by means of which the final pressure p_3 and final quality x_3 may be calculated.

SUGGESTION. The total energy remains unchanged, and the volume of the final mixture is the sum of the volumes of the original constituents.

24. Let 1 lb. of mixture at a pressure of 20 lb. per square inch, quality 0.96, enter a condenser which contains 20 lb. of mixture at a pressure of 3 in. Hg., quality 0.05. Assuming that no heat leaves the condenser during the process, find the pressure and quality after mixing.

25. One vessel contains 1 lb. of steam at a pressure of 160 lb. per sq. in. and a temperature of 420° F.; another vessel contains 4 lb. of steam at 80 lb. pressure and quality of 0.95. Show that if the vessels are placed in communication the final pressure will be 91.9 lb. per sq. in. and the final quality 0.995. Calculate the increase of entropy due to the mixing. Why should there be an increase of entropy?

26. A mixture of steam and water has the quality $x = 0.5$ and a temperature of 195° F. If the steam is compressed adiabatically will the quality increase or decrease? If the temperature is 350° F. instead of 195° how will the quality change?

27. It has been suggested that the curve of adiabatic expansion in pv-coordinates may be represented approximately by the equation $pv^n = \text{const.}$ In the four adiabatic expansions in Ex. 6, find v_1 and v_2 and from the assumed relation $p_1v_1^n = p_2v_2^n$ determine the exponent n. Then calculate the external work from the formula ${}_1W_2 = \dfrac{p_1v_1 - p_2v_2}{n-1}$ and compare the results with the results obtained from the accurate method.

28. Find the following from the Mollier chart.

(*a*) Saturated steam at 150 lb. pressure expands adiabatically to 15 lb. pressure; what is the final quality x_2?

(*b*) What is the final quality when steam at a pressure of 200 lb. per sq. in. and temperature of 550° expands adiabatically to a pressure of 2 lb. per sq. in.?

(*c*) Find the decrease in thermal potential i in these cases.

(*d*) Steam at a pressure of 150 lb. per sq. in. and quality 0.96 expands

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along a const.-i line to a pressure of 10 lb. per sq. in. What is the final condition of the steam?

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CHAPTER IX

THE FLOW OF FLUIDS

101. Preliminary Statement.—Under the title "flow of fluids" are included all motions of fluids that progress continuously in one direction, as distinguished from the oscillating motions that characterize waves of various kinds. Important examples of the flow of elastic fluids are the following: (1) The flow in long pipes or mains, as in the transmission of illuminating gas or of compressed air. (2) The flow through moving channels, as in the centrifugal fan. (3) The flow through orifices and tubes or nozzles. The recent development of the steam turbine has made especially important a study of the last case, namely, the flow of steam through orifices and nozzles.

Of the early investigators in the field under discussion, mention may be made of Daniel Bernoulli (1738), Navier (1829), and of de Saint Venant and Wantzel (1839). The latter deduced the rational formulas that to-day lie at the foundation of the theory of flow; they further stated correctly conditions for maximum discharge, and advanced certain hypotheses regarding the pressure in the flowing jet which were at the time disputed but which have since been proved valid.

Extensive and important experiments on the flow of air were made by Weisbach (1855), Zeuner (1871), Fliegner (1874 and 1877), and Hirn (1844). These served to verify theory and afforded data for the determination of friction coefficients. In 1897 Zeuner made another series of experiments on the flow of air through well-rounded orifices.

Experiments on the flow of steam were made by Napier (1866), Zeuner (1870), Rosenhain (1900), Rateau (1900), Gutermuth and Blaess (1902, 1904).

Most of the experimental work here noted relates to the flow of fluids through simple orifices or through short convergent tubes. The more complicated relations between velocity, pres-

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sure, and sectional area that obtain for flow through relatively long diverging nozzles have been investigated experimentally by Stodola, while the theory has been developed by H. Lorenz and Prandtl. The flow of steam through turbine nozzles has also been discussed by Zeuner.

102. Assumptions.—In order to simplify the analysis of fluid flow and render possible the derivation of fundamental equations, certain assumptions and hypotheses must necessarily be made.

1. It is assumed that the fluid particles move in non-intersecting curves—stream lines—which in the case of a prismatic channel may be considered parallel to the axis of the channel. We may imagine surfaces stretched across the channel, as F, F', F'', etc., Fig. 33, to which the stream lines are normal. These are the cross sections of the channel. They are not necessarily plane surfaces, but they may usually be so assumed with sufficient accuracy.

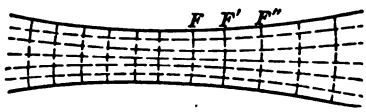


FIG. 33.

2. The fluid, being elastic, is assumed to fill the channel completely. From this assumption follows the *equation of continuity*, namely:

$$Fw = Mv, \tag{1}$$

in which F denotes the area of cross section, w the mean velocity of flow across the section, M the weight of fluid passing in a unit of time, and v the specific volume.

3. It is assumed that the motion is steady. The variables p, v, T giving the state of the fluid and also the mean velocity w remain constant at any cross section F; in other words, these variables are independent of the time and depend only upon the position of the cross section.

103. First Fundamental Equation.—The general theory of flow of elastic fluids is based upon two fundamental equations, which are derived by applying the principle of conservation of energy to an elementary mass of fluid moving in the tube or channel.

Let w_1 denote the velocity with which the fluid crosses a section F_1 of a horizontal tube, Fig. 34, and w the velocity at some second section F. A unit weight of the fluid at section F_1 has the kinetic energy of motion $\frac{w_1^2}{2g}$ due to the velocity w_1;

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hence if u_1 is the intrinsic energy of the fluid at this section, the total energy is $u_1 + \frac{w_1^2}{2g}$. Likewise, the energy of a unit weight of fluid at section F is $u + \frac{w^2}{2g}$. In general, the total energy at section F is different from that at section F_1 and the change of energy between the sections must arise: (1) from energy entering or leaving the fluid in the form of heat during the passage from F_1 to F; (2) from work done on or by the fluid. The heat entering the fluid per unit of weight between the two sections may be denoted by q. The only source of external work is at the sections F_1 and F. As a unit weight of fluid passes section F_1, a unit weight also passes section F. Denoting by p_1 and v_1 the pressure and specific volume, respectively, at F_1, the work done *on* a unit weight of fluid in forcing it across section F_1 is the product p_1v_1; similarly, the product pv gives the work done *by* a unit weight of fluid at section F on the fluid preceding it. For each unit weight flowing the net work *received* is, therefore,

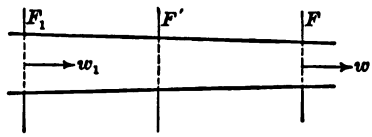


FIG. 34.

$$p_1v_1 - pv.$$

Equating the change of energy between F_1 and F to the energy received from external sources, we obtain

$$\left(u + \frac{w^2}{2g}\right) - \left(u_1 + \frac{w_1^2}{2g}\right) = Jq + p_1v_1 - pv,$$

or
$$\frac{w^2 - w_1^2}{2g} = Jq + (u_1 + p_1v_1) - (u + pv). \tag{1}$$

In many cases the heat q entering or leaving the flowing fluid is negligible, that is, the flow is adiabatic. The sum $u + pv$ will be recognized as Ji, that is, the work equivalent of the thermal potential i. For adiabatic flow the preceding equation may therefore be written in the form

$$\frac{w^2 - w_1^2}{2g} = J(i_1 - i), \tag{2}$$

or in the form

$$\frac{w_1^2}{2g} + Ji_1 = \frac{w^2}{2g} + Ji. \tag{3}$$

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It appears from these equations that Ji is analogous to the head h in hydraulics; for this reason we may call it the *thermal head*, and equation (3) may be interpreted as follows: *In adiabatic flow the sum of the velocity head and thermal head is the same at all cross sections of the channel.*

In the case of flow from a boiler or reservoir through an orifice or a nozzle the section F_1 may be taken in the vessel, in which case the velocity w_1 is negligible compared with the velocity w. Equation (2) thereupon becomes

$$\frac{w^2}{2g} = J(i_1 - i), \tag{4}$$

or

$$w = \sqrt{2gJ}\sqrt{i_1 - i} = 223.7\sqrt{i_1 - i}. \tag{5}$$

104. Frictional Resistance.—In the flow of a fluid along a channel certain frictional resistances are encountered. When the motion is turbulent there is internal fluid friction, the amount of which depends on the viscosity of the fluid; however, the greater part of the resistance is doubtless due to the friction between the moving fluid and the walls of the channel or tube.

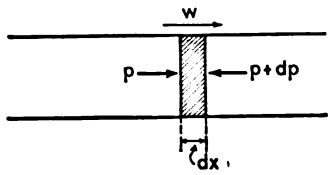


FIG. 35.

Experiments indicate that the frictional resistance varies approximately with the density of the fluid, the square of the velocity, and the rubbing surface. Suppose a lamina of the fluid of width dx, Fig. 35, to move with the velocity w. Let P denote the perimeter of the pipe ($P = \pi d$ for a pipe of circular cross section); then the rubbing surface is Pdx. Let dz denote the frictional resistance, and γ the density of the fluid. Then the expression for dz is

$$dz = \zeta\gamma\frac{w^2}{2g}Pdx, \tag{1}$$

in which ζ is a coefficient to be determined by experiment.

105. Second Fundamental Equation.—The pressure along the channel is, in general, different at different sections and decreases in the direction of flow. Denoting by p the pressure on the left hand face of the lamina, Fig. 35, and by $p + dp$ the pressure on the right hand face, it will be observed that dp is intrinsically negative. If F denotes the area of the cross section, $-Fdp$ is the

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force urging the lamina along the pipe, and the work done in moving the lamina through the distance dx is $-Fdp\ dx$. This work is expended in overcoming the frictional resistance z and in giving the lamina additional kinetic energy. The weight of the lamina is $\gamma F dx$, and the kinetic energy is therefore $\gamma F dx \frac{w^2}{2g}$. The increase of kinetic energy when the velocity increases to $w + dw$ is

$$\gamma F dx\ d\left(\frac{w^2}{2g}\right) = \gamma F dx \frac{wdw}{g};$$

and the work done against friction is

$$dzdx = \zeta\gamma \frac{w^2}{2g} P dx\ dx.$$

The equation of work applied to the lamina is therefore

$$-Fdp\ dx = \gamma F dx \frac{wdw}{g} + \zeta\gamma \frac{w^2}{2g} P dx\ dx, \tag{1}$$

or

$$\frac{dp}{\gamma} + \frac{wdw}{g} + \zeta \frac{w^2}{2g} \frac{P}{F} dx = 0. \tag{2}$$

The ratio F/P is the hydraulic mean radius of the channel, which may be denoted by m. For $\frac{1}{\gamma}$ we may substitute the specific volume v. Equation (2) therefore becomes

$$vdp + \frac{wdw}{g} + \frac{\zeta}{m} \frac{w^2}{2g} dx = 0. \tag{3}$$

In the case of a pipe of circular cross section $m = \frac{1}{4}\pi d^2/\pi d = \frac{1}{4}d$, and (3) becomes

$$vdp + \frac{wdw}{g} + \frac{4\zeta}{d} \frac{w^2}{2g} dx = 0. \tag{4}$$

Equation (3) is the second fundamental equation of flow. It is useful in the investigation of flow through long pipes.

106. Graphical Representations.—In the case of flow through orifices or short tubes the pressure drops rapidly in a short distance and the energy of the flowing fluid increases correspondingly. From the two fundamental equations we may develop instructive graphical representations, in which the change of kinetic energy and the effect of friction on this change are clearly shown.

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In all cases it is assumed that the flow is adiabatic. The first fundamental equation is then

$$\frac{w_2^2 - w_1^2}{2g} = J(i_1 - i_2), \tag{1}$$

and this holds equally well for frictionless flow and for flow with friction. The effect of friction is to decrease the kinetic energy $w_2^2/2g$ and correspondingly increase the thermal head Ji_2. If the flow is frictionless, the second fundamental equation becomes

$$vdp + \frac{wdw}{g} = 0,$$

whence

$$\frac{w_2^2 - w_1^2}{2g} = -\int_{p_1}^{p_2} vdp. \tag{2}$$

Let the curve AB, Fig. 36, represent the relation between the pressure and volume of the flowing fluid as the pressure falls from p_1 at section F_1 to p_2 at section F_2. The area $ABCD$ between the curve and the p-axis is given by the integral

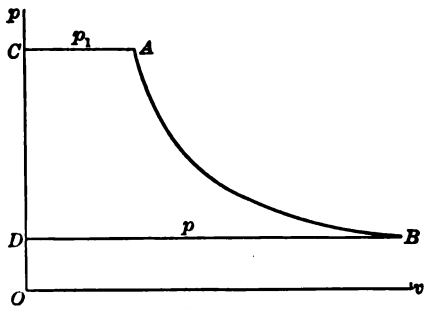


FIG. 36.

$$\int_{p_2}^{p_1} vdp = -\int_{p_1}^{p_2} vdp; \tag{3}$$

Therefore, in the case of frictionless flow, this area represents the increase of the kinetic energy of a unit weight of the fluid.

If the fluid is a permanent gas, as air, the curve AB has the equation of the adiabatic, namely

$$pv^k = p_1v_1^k = p_2v_2^k = C. \tag{4}$$

Making use of this relation, we have

$$\int_{p_2}^{p_1} vdp = C^{\frac{1}{k}} \int_{p_2}^{p_1} p^{-\frac{1}{k}}\, dp = \frac{C^{\frac{1}{k}}}{1 - \frac{1}{k}} \left({p_1}^{1-\frac{1}{k}} - {p_2}^{1-\frac{1}{k}} \right).$$

But $C^{\frac{1}{k}} = p_1^{\frac{1}{k}} v_1 = p_2^{\frac{1}{k}} v_2$, and introducing these values in the parenthesis, we get

$$\frac{w_2^2 - w_1^2}{2g} = \int_{p_2}^{p_1} vdp = \frac{k}{k-1}(p_1v_1 - p_2v_2). \tag{5}$$

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Since for a gas $Ji = \frac{k}{k-1} pv$, the second member of (5) is the difference $Ji_1 - Ji_2$, which is in agreement with equation (1).

If the fluid is a mixture of vapor and liquid or a superheated vapor, representation on the temperature entropy plane is more convenient. Let A, Fig. 37, represent the initial state of the mixture the initial pressure p_1; then the frictionless adiabatic change of state is represented by the line AB parallel to the T-axis. The area $DCAB$ represents the change of thermal potential $i_1 - i_2$ between A and B; therefore from Equation (1)

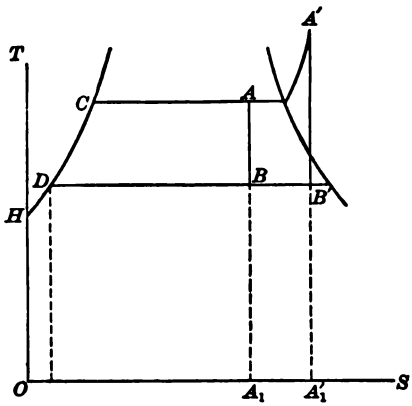


FIG. 37.

$$\frac{w_2^2 - w_1^2}{2g} = J \times \text{area } DCAB. \qquad (6)$$

If the vapor is initially superheated as indicated by the point A', the change of state is represented by $A'B'$ and the area $DCA'B'$ represents the increase of kinetic energy.

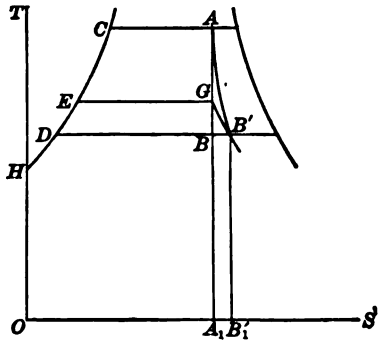


FIG. 38.

The effect of friction is easily shown. The work done in overcoming the frictional resistances is transformed into heat H, and therefore the entropy of the fluid must be increased by the amount

$$s_2 - s_1 = \int_1^2 \frac{dH}{T}. \qquad (7)$$

The curve representing the change of state must lie to the right of the frictionless adiabatic AB in some such position as AB', Fig. 38, the segment BB' is given by (7), and the area $A_1AB'B_1'$, represents the heat H.

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Let the first fundamental equation be applied successively to the changes represented by AB and AB'. We have

$$\frac{w_1^2}{2g} + Ji_1(\text{at } A) = \frac{w_2^2}{2g} + Ji_2 \text{ (at } B),$$

$$\frac{w_1^2}{2g} + Ji_1 \text{ (at } A) = \frac{w_2'^2}{2g} + Ji_2' \text{ (at } B').$$

Hence
$$\frac{w_2^2}{2g} + Ji_2 = \frac{w_2'^2}{2g} + Ji_2',$$

or
$$\frac{w_2^2 - w_2'^2}{2g} = J(i_2' - i_2). \tag{8}$$

The area $A_1BB'B'_1$ represents $i'_2 - i_2$, and when expressed in mechanical units it therefore represents the decrease of kinetic energy due to friction.

Through B' let a constant-i line be drawn intersecting AB in the point G. Then the thermal head at G is i'_2, and the area $ECAG$ represents the difference $i_1 - i_2'$ which gives the increase of kinetic energy when friction is present. The loss of kinetic energy due to friction is therefore represented by the area $DEGB$.

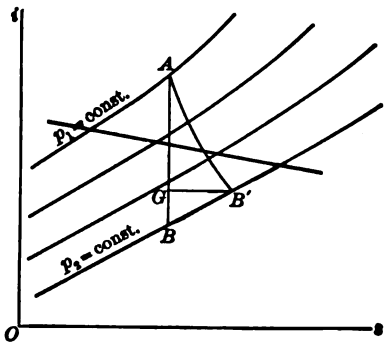


FIG. 39.

The most convenient graphical representation for practical purposes is obtained by taking the thermal head i and entropy s as coördinates. On this plane a series of constant pressure lines are drawn, Fig. 39; then a vertical segment AB represents a frictionless adiabatic change from pressure p_1 to a lower pressure p_2, while a curve AB' between the same pressure limits represents an expansion with increasing entropy, that is, one with friction. The segment AB, therefore, represents the increase of jet energy $\frac{w_2^2 - w_1^2}{2g}$ without friction, the segment AG, the smaller increase $\frac{w_2'^2 - w_1^2}{2g}$ with friction, and the segment GB, the decrease in final kinetic energy due to friction.

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The ratio GB/AB, that is, the ratio of the loss of kinetic energy to the increase of kinetic energy without friction, is denoted by the symbol y. We have therefore

$$AG = (1 - y)AB$$

or
$$\frac{w_2'^2 - w_1^2}{2g} = (1 - y)\frac{w_2^2 - w_1^2}{2g}. \tag{9}$$

If w_1 is taken as zero, as in the case of flow from a boiler, then

$$\frac{w_2'^2}{2g} = (1 - y)\frac{w_2^2}{2g} = J(1 - y)(i_1 - i_2),$$

or
$$w_2' = 223.7\sqrt{(1 - y)(i_1 - i_2)}. \tag{10}$$

107. Discharge through Orifices and Short Tubes.—Consider the flow of a fluid from a reservoir in which the pressure is p_1 through an orifice or short tube, Fig. 40, into a region in which exists a pressure p_2 lower than p_1. The section F_1 is taken in the reservoir and the velocity w_1 may therefore be taken as zero. The section F is taken at the end of the tube, and the pressure at that section is denoted by p. The relation between the pressures p and p_2 is one of the subjects of the investigation.

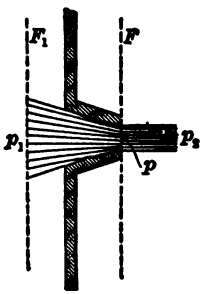


FIG. 40.

Let the fluid be air or other permanent gas, and suppose the flow to be adiabatic and frictionless. Then from equation (5) of the preceding article, taking $w_1 = 0$,

$$\frac{w^2}{2g} = \frac{k}{k - 1}(p_1v_1 - pv). \tag{1}$$

Let M denote the weight of fluid discharged per second, F the area of the cross section, and v the volume per pound as the fluid crosses the section F; then

$$Fw = Mv. \tag{2}$$

Eliminating w between (1) and (2), the discharge M is given by the equation

$$M = \frac{F}{v}\sqrt{2g\frac{k}{k - 1}(p_1v_1 - pv)}. \tag{3}$$

From the adiabatic relation

$$pv^k = p_1v_1^k$$

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we have $$v = v_1 \left(\frac{p_1}{p}\right)^{\frac{1}{k}},$$

and introducing this expression for v in (3), we obtain after reduction

$$M = F\sqrt{2g\frac{k}{k-1}\frac{p_1}{v_1}\left[\left(\frac{p}{p_1}\right)^{\frac{2}{k}} - \left(\frac{p}{p_1}\right)^{\frac{k+1}{k}}\right]}. \qquad (5)$$

This equation gives a relation between the discharge M and the pressure p at the end of the tube.

108. Critical Pressure. Maximum Discharge.—An inspection of the equation for the discharge M shows that M reduces to

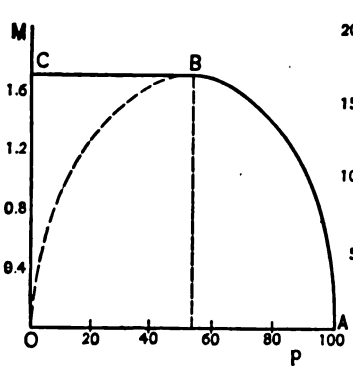


FIG. 41.

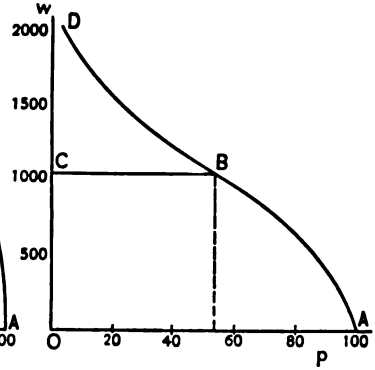


FIG. 42.

zero when $p = p_1$ and also when $p = 0$. The general course of the curves of discharge and velocity plotted against p as abscissa is shown in Fig. 41 and 42. These curves were calculated from the following data:

Fluid	air.
Reservoir pressure p_1	100 lb. per sq. in.
Area F of end section of tube	0.005 sq. ft.

For various assumed values of p, the calculated values of w and M are:

p =	0	10	20	40	60	80	90	100	lb. per sq. in.
w =	2524	1752	1524	1211	930	628	435	0	ft. per sec.
M =	0	0.86	1.25	1.60	164	136	103	0	lb. per sec.

It is seen that the discharge M has a maximum value at a pressure between 50 and 60 lb. per sq. in. The exact location

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of this maximum may be found from equation (5) preceding. Evidently M is a maximum when the term

$$\left(\frac{p}{p_1}\right)^{\frac{2}{k}} - \left(\frac{p}{p_1}\right)^{\frac{k+1}{k}}$$

is a maximum. By the usual method of equating the first derivative to zero, the ratio of pressures that makes this expression a maximum is found to be

$$\frac{p}{p_1} = \left(\frac{2}{k+1}\right)^{\frac{k}{k-1}}. \qquad (1)$$

For air, taking $k = 1.4$, the ratio is 0.5283, or approximately 0.53; hence the maximum discharge is attained when the pressure p at the orifice is 53 per cent. of the pressure p_1 in the reservoir. The value of the pressure p that gives maximum discharge is denoted by p_m and is called the **critical pressure.**

When p is taken less than p_m the discharge is smaller, and ultimately when p is taken as zero M also becomes zero. It is manifestly absurd that the discharge into a vacuum should be zero, notwithstanding the fact that the equation seems to indicate such a result. The hypothesis was advanced by de Saint-Venant and Wantzel, who first derived the general equation of discharge, that the discharge into a vacuum cannot be less than the maximum discharge. The hypothesis has been fully confirmed by the experiments of Fliegner, Zeuner, and Gutermuth. The apparent contradiction between theory and experiment lies in the assumption that the pressure p at the orifice coincides with the pressure p_2 however low p_2 may be. Experiments show that $p = p_2$ as long as p_2 is greater than the critical pressure p_m, but that when p_2 drops below p_m the pressure p at the orifice remains at the value p_m. Consequently for all values of p_2 less than p_m the weight of fluid flowing per second is the same. The curve of discharge, Fig. 41, has therefore two branches, AB and BC. The ordinates of the branch AB are the values of M calculated from (5) taking the back pressure p_2 as the pressure at the orifice. The constant discharge indicated by the straight line BC is the value of M obtained when the critical pressure p_m is taken as the pressure at the orifice.

Similarly, the curve of velocity has the two parts; the curve AB shows the increasing velocity as the back pressure is lowered

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from p_1 to p_m, and the straight line BC shows the constant velocity w_m through the orifice for all values of p_2 less than p_m. The ordinates of the branch BD represent the higher velocities that an element of fluid may attain after passing beyond the orifice.

By a combination of equation (1) with the equations of velocity and discharge, expressions for the maximum velocity at the orifice and the maximum discharge may be obtained. Denoting by w_m the maximum velocity and by v_m the specific volume of the fluid at the critical pressure p_m, we have

$$\frac{w_m^2}{2g} = \frac{k}{k-1}(p_1v_1 - p_mv_m), \tag{2}$$

$$p_1v_1^k = p_mv_m^k, \tag{3}$$

and

$$p_m = p_1\left(\frac{2}{k+1}\right)^{\frac{k}{k-1}}. \tag{4}$$

From (3) and (4), we obtain

$$p_1v_1 = \frac{k+1}{2}p_mv_m. \tag{5}$$

Combining (2) and (5) the following expressions for w_m are obtained:

$$w_m = \sqrt{2g\frac{k}{k+1}p_1v_1}, \tag{6}$$

$$w_m = \sqrt{gkp_mv_m}. \tag{7}$$

The last equation expresses the fact that the maximum velocity w_m is equal to the velocity of sound in the fluid when in the state p_m,v_m. See any text book on physics. For this reason w_m is often called the **acoustic velocity.**

The maximum discharge M_m is given by the continuity equation

$$M_mv_m = Fw_m. \tag{8}$$

From (3) $$\frac{1}{v_m} = \frac{1}{v_1}\left(\frac{p_m}{p_1}\right)^{\frac{1}{k}} = \frac{1}{v_1}\left(\frac{2}{k+1}\right)^{\frac{1}{k-1}};$$

therefore we have

$$M_m = \frac{Fw_m}{v_m} = \frac{F}{v_1}\left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}w_m$$

$$= F\left(\frac{2}{k+1}\right)^{\frac{1}{k-1}}\sqrt{2g\frac{k}{k+1}\frac{p_1}{v_1}}. \tag{9}$$

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109. Fliegner's Equations for Air.—By the introduction of the temperature of the air in the reservoir the preceding equation for maximum discharge can be simplified. From the equation

$$p_1 v_1 = BT_1$$

we have

$$\frac{p_1}{v_1} = \frac{{p_1}^2}{BT_1}, \tag{1}$$

and inserting this expression in equation (9) preceding, the result is

$$M_m = \left(\frac{2}{k+1}\right)^{\frac{1}{k-1}} \left[\frac{2g}{B}\frac{k}{k+1}\right]^{\frac{1}{2}} \frac{Fp_1}{\sqrt{T_1}}. \tag{2}$$

Taking the numerical values of k and B for air, we obtain

$$M_m = 0.53 \frac{Fp_1}{\sqrt{T_1}}. \tag{3}$$

This equation gives the discharge of air through an orifice whose area is F when the back pressure p_2 is less than the critical pressure p_m. It applies to other gases with an appropriate change of the constant. As regards the units to be used, the pressure p_1 is taken in pounds per square inch when F is expressed in square inches, and in pounds per square foot when F is in square feet. The discharge is expressed in pounds per second.

When the back pressure p_2 exceeds the critical pressure p_m, the discharge may be calculated from the general equation (5) Art. 107, by the substitution of p_2 for p. When the equation is simplified and the numerical values of k and B are inserted the equation takes the form

$$M = 2.056 \frac{Fp_1}{\sqrt{T_1}} \sqrt{\left(\frac{p_2}{p_1}\right)^{\frac{10}{7}} - \left(\frac{p_2}{p_1}\right)^{\frac{12}{7}}}. \tag{4}$$

Experiments on the flow of air have been made by Fliegner, Weisbach, and Zeuner. In Fliegner's experiments air flowed from a reservoir in which the pressure was p_1 into the atmosphere. Two well-rounded orifices having diameters of 4.085 and 7.314 mm. at the throat were used. The equations deduced by Fliegner to represent the experimental results were:

When $p_1 > 2p_a$ $\quad M = 0.53 \frac{Fp_1}{\sqrt{T_1}}$. (5)

When $p_1 < 2p_a$ $\quad M = 1.06 \frac{F}{\sqrt{T_1}} \sqrt{p_a(p_1 - p_a)}$. (6)

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In these equations p_a denotes atmospheric pressure, 14.7 lb. per sq. in.

The first equation agrees exactly with equation (3) for maximum discharge; the second equation, however, differs from the rational equation (4). To determine the amount of the discrepancy between (4) and (6), we equate the two expressions for M, leaving out the common factors and substituting c for the constant 1.06. Thus

$$2.056\, p_1\sqrt{\left(\frac{p_2}{p_1}\right)^{\frac{10}{7}} - \left(\frac{p_2}{p_1}\right)^{\frac{12}{7}}} = c\sqrt{p_2(p_1 - p_2)}.$$

For different values of the ratio p_2/p_1 we obtain the following values of c.

p_2/p_1	0.5	0.6	0.7	0.8	0.9
c	1.061	1.073	1.081	1.088	1.093

It appears, therefore, that Fliegner's equation (6) gives a discharge that is one to three per cent. less than the discharge given by (4). The use of (6) rather than (4) amounts to the assumption of a coefficient of discharge of 97 to 99 per cent.

110. Flow of Steam.—The weight of steam flowing through an orifice or short tube may be calculated from the two equations

$$w = 223.7\sqrt{i_1 - i_2}, \tag{1}$$

$$M = \frac{Fw}{v}. \tag{2}$$

It is assumed that the flow is adiabatic and frictionless; hence the entropy of the steam in the state it assumes at the orifice is equal to the initial entropy. The volume v in (2) is, of course, the specific volume in the second state.

If the pressure p_2 of the region into which the steam is discharging exceeds the critical pressure, the thermal head i_2 corresponding to this pressure is used in (1) and the corresponding volume v_2 in (2); but if p_2 is less than the critical pressure p_m, the velocity in the plane of the orifice is given by

$$w_m = 223.7\sqrt{i_1 - i_m}, \tag{3}$$

and the maximum discharge by

$$M_m = \frac{Fw_m}{v_m}. \tag{4}$$

For steam the critical ratio varies somewhat with the pressure

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and quality or superheat. The following values may be taken as sufficiently accurate:

For steam highly superheated p_m/p_1 =	0.55.
For steam moderately superheated	0.56–0.57.
For saturated or wet steam	0.58

EXAMPLE. Saturated steam at a pressure of 150 lb. per sq. in. flows through an orifice whose area is 0.32 sq. in. Find the discharge in pounds per minute (*a*) when the back pressure p_2 is 110 lb. per sq. in., (*b*) when p_2 is 30 lb. per sq. in.

From the steam table $i_1 = 1194.7$ B. t. u. and $s_1 = 1.5704$. The quality of steam at 100 lb. to have the same entropy is determined from the equation

$$1.5704 = s_2' + x_2 \frac{r_2}{T_2} = 0.4827 + 1.1138\,x,$$

from which $x = 0.976$. Therefore $i'_2 = i''_2 - (1 - x)r_2 = 1190.0 - 0.024 \times 884.6 = 1168.8$ B. t. u., and $v_2 = xv''_2 = 0.976 \times 4.057 = 3.948$ cu. ft.

$$w = 223.7\sqrt{1194.7 - 1168.8} = 1133 \text{ ft. per sec.}$$

$$M = F\frac{w}{v} = \frac{0.32}{144} \times \frac{1133}{3.948} = 0.638 \text{ lb. per sec.} = 38.3 \text{ lb. per min.}$$

In the second case p_2 is less than p_m, which is $150 \times 0.58 = 87$ lb. per sq. in.; hence x, i, and v for 87 lb. must be used. The following values are found: $x_m = 0.961$, $i_m = 1150.9$, $v_m = 4.86$. Then

$$w_m = 223.7\sqrt{1194.7 - 1150.9} = 1480 \text{ ft. per sec.,}$$

and

$$M_m = \frac{0.32}{144} \times \frac{1480}{4.86} \times 60 = 40.6 \text{ lb. per min.}$$

The pressure-entropy table for steam[1] may be used to advantage in calculations of the flow of steam. The following example illustrates the method to be followed.

EXAMPLE. Find the area of orifice required for the discharge of 33 lb. per min. of steam at 200 lb. pressure and superheated to 540° F.

Following the line $p = 200$, it is found that for $s = 1.64$, $t = 530°$, and for $s = 1.65$, $t = 548.3$; hence for $t = 540°$, $s = 1.6455$, and $i_1 = 1284.6 + 0.55 \times 10 = 1290.1$. The critical pressure p_m is $0.55 \times 200 = 110$, and for this pressure $i_m = 1225.9 + 0.55 \times 8.7 = 1230.7$, and $v_m = 4.475 + 0.55 \times 0.082 = 4.52$. $w_m = 223.7\sqrt{1290.1 - 1230.7} = 1724$, and

$$F = \frac{Mv}{w} = \frac{33}{60} \times \frac{4.52}{1724} = 0.00144 \text{ sq. ft.} = 0.208 \text{ sq. in.}$$

[1] Properties of Steam and Ammonia, p. 110.

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111. Empirical Formulas.—Various formulas have been proposed for the maximum discharge of steam through an orifice. The simplest is that of Napier, namely

$$M = \frac{Fp}{70}. \tag{1}$$

Grashof's formula is

$$M = 0.0165\, Fp^{0.97}. \tag{2}$$

Rateau has proposed the formula

$$M = \frac{Fp}{1000}(16.367 - 0.96 \log p). \tag{3}$$

as representing the results of his experiments.

In these three formulas p is the pressure in the boiler or reservoir in pounds per square inch, F the area of the orifice in square inches, and M the discharge in pounds per second. The formulas apply to maximum discharge only, that is to the case when p_2 is less than the critical pressure.

Napier's formula is inaccurate especially if the steam is superheated; it is, however, useful as a check. The other formulas present no advantages over the exact method of calculation given in the preceding article.

112. The de Laval Nozzle.—The character of the flow through a simple orifice depends largely upon the pressure p_2 in the region into which the jet passes. There are two cases to be discussed: 1. When p_2 is equal to or greater than the critical pressure p_m. 2. When p_2 is less than p_m.

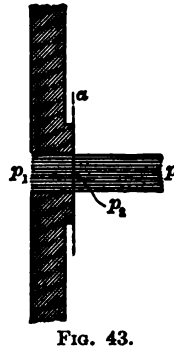


FIG. 43.

In the first case the pressure at the cross section a, Fig. 43, takes the value p_2 of the surrounding region, and the jet experiences no change of pressure as it passes into the region beyond the nozzle. There is no tendency, consequently, for the jet to spread laterally, and for some distance beyond the orifice it will have practically constant cross section. Furthermore, since there is no drop in pressure along the axis of the jet, the velocity remains practically constant at successive cross sections. This velocity is given by (1) Art. 110.

In the second case the pressure at section a takes the critical value p_m, which is greater than the pressure of the surroundings.

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As a result of the pressure difference $p_m - p_2$, the jet will expand laterally, as shown in Fig. 44. Furthermore, along the axis of the jet the pressure drops continuously from its initial value p_m until at some distance from the orifice it attains the pressure p_2. Hence, due to this pressure drop, the velocity of the jet in the direction of the axis will increase as successive sections are passed.

Referring to Fig. 42, the velocity at section a is the ordinate of the line BC, and the increasing velocity as the pressure drops from p_m to p_2 is shown by the ordinate of the curve BD.

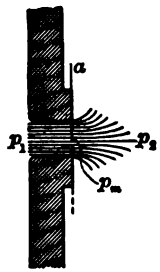


FIG. 44.

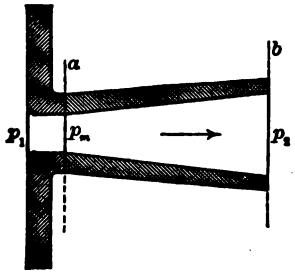


FIG. 45.

The lateral spreading of the jet may be prevented by adding to the orifice a properly proportional tube, as shown in Fig. 45. The orifice and tube together constitute a nozzle. The tube must diverge so as to permit the expansion of the fluid required by the drop of pressure from p_m at section a to p_2 at section b; and the area of the end section b depends upon the final pressure p_2. At section a the jet has the acoustic velocity w_m as if the added tube were not present. As the jet proceeds along the tube the velocity increases, and at the end section b takes the value

$$w_2 = 223.7\sqrt{i_1 - i_2}.$$

113. Friction in Nozzles.—In the case of flow through a simple orifice or through a short convergent tube with rounded entrance, the friction between the jet and orifice, or tube, is small and scarcely demands attention. With the divergent de Laval nozzle, on the contrary, the friction may be considerable and must be taken into account. As explained in Art. 106, the effect of friction is to produce a decrease in the jet energy $\frac{w_2^2}{2g}$

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at the end section. Thus if w'_2 is the final velocity and y the coefficient of energy loss,

$$\frac{w'^2_2}{2g} = (1 - y)\frac{w_2^2}{2g}. \tag{1}$$

and

$$w'_2 = 223.7\sqrt{(1 - y)\,(i_1 - i_2)}. \tag{2}$$

Another effect of friction is the increase of the specific volume v of the fluid at a given cross section of the nozzle. Referring to Fig. 38, the point B' that represents the state of the fluid at pressure p_2 when there is friction indicates a higher quality and therefore a greater volume than the point B that represents the final state in the case of frictionless flow. The increase of quality arises from the absorption by the fluid of the heat generated in overcoming the frictional resistances.

From the equation of continuity

$$F = M\frac{v}{w}, \tag{3}$$

it appears that the effect of friction is to increase the numerator v and decrease the denominator w of the fraction of the second member; hence for a given discharge M, the cross section F must be larger the greater the friction, that is, for the same lower pressure p_2.

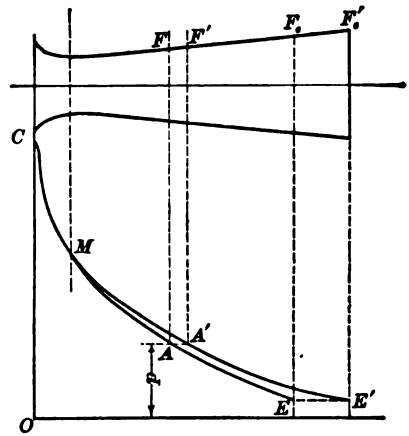


FIG. 46.

The effect of friction may be viewed from another aspect. In Fig. 46 let the curve $CMAE$ represent the pressures along the axis of a de Laval nozzle on the assumption of no friction. This curve is readily found for a given value of p_1 by finding for various lower pressures p the proper cross section F by means of the two equations,

$$\frac{w^2}{2g} = J(i_1 - i), \text{ and } F = \frac{Mv}{w}.$$

Let A be a point on the pressure curve obtained in this manner. If now friction is taken into account, the section F' associated

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with the lower pressure p has a larger area than the section F calculated on the assumption of no friction; therefore, the point A is shifted by friction to a new position A' underneath the new section F'. Similarly the end section F_e must be increased in area to F'_e, and the point E on the frictionless pressure curve is shifted to a new position E'. The effect of the friction, therefore, is to raise the pressure curve as a whole, that is, to increase the pressure at any point in the axis of the nozzle.

114. Design of Nozzles.—The diverging part of a nozzle is usually conical; the angle between the sides may be varied somewhat but 10° is a value frequently used. For a given discharge of steam the areas of two sections must be calculated; the throat, where the pressure may be taken as the critical pressure p_m, and the end section, which should have the area appropriate to the back pressure p_2. With a well-rounded entrance the frictional resistance up to the throat may be regarded as negligible, and the throat area may be calculated upon the assumption that the flow is frictionless. The friction in the divergent part is taken account of by the coefficient y.

In the calculation of the two areas the thermal quantities required may be obtained from the Mollier chart or from the pressure-entropy table. The following example illustrates the method to be followed.

EXAMPLE. A nozzle is to deliver 12 lb. of steam per minute; the steam is initially saturated at a pressure of 135 lb. per sq. in., and the back pressure is 30 in. of mercury. The coefficient y may be taken as 0.10.

The critical pressure is $135 \times 0.58 = 78.3$ lb. Since a small variation of this pressure makes no appreciable difference in the discharge, 78 lb. may be taken. From the steam table we find for the initial conditions $i_1 = 1193.2$ B. t. u., $s_1 = 1.5793$; and from the pressure-entropy table, the values of i_m and v_m for $s = 1.5793$ and $p = 58$ are found to be $i_m = 1149.0$ B. t. u. and $v_m = 5.39$ cu. ft. Hence

$$w_m = 223.7\sqrt{1193.2 - 1149.0} = 1487 \text{ ft. per sec.}$$

and

$$F_m = M\frac{V_m}{w_m} = \frac{12}{60} \times \frac{5.39}{1487} = 0.000725 \text{ sq. ft.} = 0.1044 \text{ sq. in.}$$

The area at the throat may be checked by Napier's rule; thus

$$F = \frac{70\,M}{p_1} = \frac{70}{135} \times \frac{12}{60} = 0.1037 \text{ sq. in.}$$

To get the area of the end section F_2, we assume first frictionless flow and find for $s = 1.5793$ and $p = 30$ in. of mercury $i_2 = 1031.3$ B. t. u. The

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decrease of thermal head, without friction, is 1193.2 − 1031.3 = 161.9 B. t. u. If y is 0.10 this is reduced by 16.2 B. t. u., leaving 145.7 available for increasing the energy of the jet. Therefore the velocity w_2 at the end section is

$$w_2 = 223.7\sqrt{145.7} = 2700 \text{ ft. per sec.}$$

Because of friction the thermal head at the pressure p_2 is increased by 16.2 B. t. u. and is therefore 1031.3 + 16.2 = 1047.5 B. t. u. In the pressure-entropy table, opposite 30 in. of mercury, we find the values

s =	1.60	1.61
i =	1045.2	1051.9
v =	23.81	23.99

By interpolation the value of v corresponding to 1047.5 B. t. u. is found to be 23.89 cu. ft. The area required is therefore

$$F_2 = M\frac{v_2}{w_2} = \frac{12}{60} \times \frac{23.89}{2700} = 0.00177 \text{ sq. ft.} = 0.2548 \text{ sq. in.}$$

The corresponding diameters are

$$d_m = 0.363 \text{ in.} \qquad d_2 = 0.570 \text{ in.}$$

If the angle of the cone is taken as 10°, the length of the diverging part is (0.570 − 0.363) ÷ 2 tan 5° = 1.18 in.

FLOW OF COMPRESSIBLE FLUIDS IN MAINS

115. Equations of Flow.—When a compressible fluid flows in a long main the pressure gradually decreases because of the frictional resistances, and if the temperature is assumed to remain constant the specific volume increases. Therefore, according to the equation of continuity, $Fw = Mv$, the velocity must increase with the volume, provided the main has a constant cross section area F.

Two equations of flow in mains may be derived from the second fundamental formula, namely

$$v dp + \frac{w dw}{g} + \frac{\zeta}{m}\frac{w^2}{2g}dx = 0. \qquad \text{[Art. 105] (1)}$$

In the first case considered the decrease of pressure is small relative to the initial pressure p_1. The changes in the volume v and velocity w are correspondingly small, and may be neglected. With this assumption (1) becomes

$$-dp = \frac{\zeta}{mv}\frac{w^2}{2g}dx, \qquad (2)$$

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and the result of integration with w and v constant is the equation

$$p_1 - p_2 = \frac{\zeta}{mv}\frac{w^2}{2g}L, \tag{3}$$

in which L denotes the length of the pipe.

In the second case the drop in pressure is so large that the approximation is not permissible; the variation of w and v must be taken into account. Taking out the factor $\frac{w^2}{2g}$, (1) becomes

$$2g\frac{vdp}{w^2} + 2\frac{dw}{w} + \frac{\zeta}{m}dx = 0. \tag{4}$$

To get the first term of this equation in integrable form, we make use of the following relations

$$\frac{1}{w} = \frac{F}{Mv}, \qquad \frac{1}{w^2} = \frac{F^2}{M^2v^2}, \qquad \frac{v}{w^2} = \frac{F^2}{M^2v}.$$

For air and other gases, $\frac{1}{v} = \frac{p}{BT}$;

hence $$\frac{v}{w^2} = \frac{F^2p}{M^2BT}.$$

Inserting this expression in the first term of (4), we have

$$\frac{2gF^2}{M^2BT}pdp + 2\frac{dw}{w} + \frac{\zeta}{m}dx = 0. \tag{5}$$

If the temperature T is taken as constant, the integration of (5) gives the equation

$$p_1^2 - p_2^2 = \frac{M^2BT}{gF^2}\left(2\log_e\frac{w_2}{w_1} + \frac{\zeta}{m}L\right). \tag{6}$$

If the pipe is long the term $2\log_e\frac{w_2}{w_1}$ is negligible in comparison with the term $\frac{\zeta}{m}L$, and the equation becomes

$$p_1^2 - p_2^2 = \zeta\frac{M^2BTL}{gF^2m}. \tag{7}$$

Let w_1 denote the initial velocity and v_1 the initial specific volume corresponding to the initial pressure p_1; then

$$F_1w_1 = Mv_1 = \frac{MBT}{p_1},$$

and $$M^2 = \frac{p_1^2F^2w_1^2}{B^2T^2}.$$

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Substituting this expression in (7) the resulting equation is

$$\frac{p_1^2 - p_2^2}{p_1^2} = \frac{\zeta w_1^2 L}{gBTm}. \tag{8}$$

From (8) the following equations are obtained:

$$p_2 = p_1 \left[1 - \frac{\zeta w_1^2 L}{gBTm}\right]^{\frac{1}{2}}, \tag{9}$$

$$w_1 = \left[\frac{gBTm}{\zeta L} \frac{p_1^2 - p_2^2}{p_1^2}\right]^{\frac{1}{2}}, \tag{10}$$

$$\zeta = \frac{gBTm}{w_1^2 L} \frac{p_1^2 - p_2^2}{p_1^2}. \tag{11}$$

Equation (9) may be used to calculate the loss of pressure for an assumed initial velocity, and conversely, (10) may be used to calculate the initial velocity for an assumed drop of pressure. Equation (11) is used to determine the coefficient ζ from experiments on flow through pipes.

It may be noted that these last equations (8)–(11) are homogeneous as regards units; the pressures may be expressed in pounds per square foot or per square inch, and the hydraulic radius m is taken in feet since L is in feet. On the other hand, equations (3) and (7) require a consistent system of units, namely: p in lb. per square foot, m and L in feet, w in feet per sec., and M in lb. per sec.

116. Coefficient of Friction.—If the frictional resistance followed exactly the law stated in Art. 104, that is, if it varied with the first power of the density and with the square of the velocity, the coefficient ζ would be constant, for all conditions of flow. It is found by experiment, however, that with the assumed expression for the frictional resistance, namely

$$dz = \zeta \gamma \frac{w^2}{2g} dx, \tag{1}$$

the coefficient ζ is not constant; it varies with the density of the fluid, the velocity, and the pipe diameter. It may be inferred, therefore, that the law expressed by (1) is only approximate; that the resistance varies with some power of γ different from 1 and with some power of w different from 2.

Probably the most elaborate and trustworthy experiments on the flow of air in pipes are those made by Fritzsche. The results

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of these experiments are expressed by the following expression for ζ:

$$\zeta = \frac{\alpha}{d^{0.269}(\gamma w)^{0.148}}, \tag{2}$$

in which d denotes the diameter of the pipe, and α is a constant whose value depends on the system of units employed. By means of the relations

$$Mv = Fw = \tfrac{1}{4}\pi d^2 w,$$

$$d^2 = \frac{4}{\pi}\frac{mv}{w} = \frac{4}{\pi}\frac{M}{\gamma w},$$

equation (2) may be reduced to the form

$$\zeta = \alpha' \frac{d^{0.027}}{M^{0.148}}. \tag{3}$$

The variation of ζ with the diameter d is so small that it may be neglected; and the exponent of M may be taken as $\frac{1}{7}$. With these modifications (3) takes the form

$$\zeta = \alpha'' M^{-\frac{1}{7}}. \tag{4}$$

For the English system of units, $\alpha'' = 0.0048$ when M is taken in pounds per second.

Unwin makes the coefficient ζ depend upon the diameter of the pipe, and has proposed the formula

$$\zeta = 0.0027\left(1 + \frac{3}{10d}\right), \tag{5}$$

in which d denotes the diameter in feet. The same formula has been applied to the flow of steam.

117. Flow of Air.—The general equation (7), Art. 115, may be used as it stands for calculating the flow of compressed air in mains; however, it may be modified as follows to suit the units usually employed.

Let V_a denote the volume of *free* air (*i.e.* air at atmospheric pressure) flowing per *minute*, then

$$M = \frac{p_a V_a}{60BT}. \tag{1}$$

Also for a circular cross section $m = \frac{1}{4}d$ and $F = \frac{1}{4}\pi d^2$. If now

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we take the pressures p_1 and p_2 in pounds per square inch, and the diameter d in inches, (7) becomes

$$p_1^2 - p_2^2 = \frac{(14.7)^2 \times (12)^5 \times 4}{(60)^2 \left(\frac{\pi}{4}\right)^2 gBT} \zeta \frac{V_a^2 L}{d^5}. \tag{2}$$

For air $B = 53.34$, and T may be given the average value 520. Inserting these values, the equation becomes

$$p_1^2 - p_2^2 = 0.1085 \zeta \frac{V_a^2 L}{d^5}. \tag{3}$$

By means of (1) we may express the coefficient ζ in terms of V_a; thus

$$\zeta = 0.0048 M^{-\frac{1}{7}} = \left(\frac{60 \times 53.34 \times 520}{144 \times 14.7}\right)^{\frac{1}{7}} \times 0.0048 V_a^{-\frac{1}{7}}$$

or

$$\zeta = 0.01245 V_a^{-\frac{1}{7}} \tag{4}$$

Combining (3) and (4), the following equations are obtained.

$$p_1^2 - p_2^2 = 0.00135 \frac{V_a^{\frac{13}{7}} L}{d^5}. \tag{5}$$

$$V_a = 35.08 \left[\frac{(p_1^2 - p_2^2) d^5}{L}\right]^{\frac{7}{13}}. \tag{6}$$

$$d = 0.267 \left(\frac{L}{p_1^2 - p_2^2}\right)^{\frac{1}{5}} V_a^{\frac{13}{35}}. \tag{7}$$

EXAMPLE. A pipe 10,000 ft. long is required to transmit 3000 cu. ft. of free air per minute; the initial pressure is 120 lb. per sq. in. and the drop in pressure is not to exceed 10 per cent. or 12 lb. Required the diameter of the pipe.

Take $p_2 = 108$ lb.; then $p_1^2 - p_2^2 = (p_1 + p_2)(p_1 - p_2) = 228 \times 12$.

$\text{Log } L = 4.00000$	$\log 0.267 = \bar{1}.42651$
$\log 228 = 2.35793$	$\frac{1}{5} \log L/(p_1^2 - p_2^2) = 0.11258$
$\log 12 = \underline{1.07918}$	$\frac{13}{35} \log V_a = \underline{1.29150}$
$\log L/(p_1^2 - p_2^2) = 0.56289$	$\log d = 0.83059$
$\log V_a = 3.47712$	$d = 6.77$ in.

If a 7-in. pipe is chosen, the drop of pressure, from (5), is 10.6 lb. per sq. in. If Unwin's equation is used, $\zeta = 0.0027 \left(1 + \frac{3.6}{7}\right) = 0.00408$ and from (3) $p_1^2 - p_2^2 = 2376$, whence $p_2 = 109.7$, and the drop of pressure is 10.3 lb. per sq. in.

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118. Flow of Steam.—In the case of steam flowing in a pipe the loss of pressure is usually small relative to the initial pressure, and the approximate equations (3) Art. 115, namely

$$p_1 - p_2 = \frac{\zeta}{mv}\frac{w^2}{2g}L, \tag{1}$$

is used. Taking $m = \frac{d}{4}$, $w = \frac{M}{F}$ $v = \frac{Mv}{\frac{1}{4}\pi d^2}$, and introducing the factor 12^2 to reduce the pressures to pounds per square inch and the diameter d from feet to inches, the equation becomes

$$p_1 - p_2 = \frac{12^2 \times 4^2 \times 4}{2g\pi^2}\zeta\frac{M^2vL}{d^5}$$

$$= 174.14\,\zeta\frac{M^2vL}{d^5}. \tag{2}$$

In the formula M denotes the weight flowing in pounds per second, and d the diameter in inches.

Values of the friction coefficient ζ for the flow of steam are not at present known accurately. The Unwin formula for air, namely

$$\zeta = 0.0027\left(1 + \frac{36}{d}\right), \quad (d \text{ in inches}) \tag{3}$$

is much used and probably gives safe results for low pressures and moderate steam velocities. For the high pressure and velocities used in modern practice, the Unwin formula is apparently not applicable. For such conditions, the experiments available point towards Fritzche's formula for air with the constant increased about 50 per cent.; thus

$$\zeta = 0.0072\ M^{-\frac{1}{7}}. \tag{4}$$

As an example consider the flow of steam at 220 lb. pressure superheated to 560° through a main 12 in. in diameter and 300 feet long. With a velocity of approximately 100 ft. per sec. the weight flowing per second is about 30 lb. Formula (3) gives $\zeta = 0.0127\left(1 + \frac{3.6}{12}\right) = 0.00351$, and formula (4) gives $\zeta = 0.0072 \times 30^{-\frac{1}{7}} = 0.00433$. Inserting these values in (2), the drop of pressure is found to be 17.7 lb. in the first case and 22.4 lb. in the second case.

119. Change of State During Flow.—Compressed air usually enters the main at a temperature considerably higher than the temperature of the surroundings, and in consequence heat flows from the air in the main to the atmosphere. In the case of

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long distance transmission the temperature of the flowing air is reduced practically to the outside temperature in a length of a few hundred feet and for the remainder of the distance the flow is at constant temperature. The changing state of the air may be represented graphically on the pv- and Ts-planes, as show in Fig. 47. The point A represents to the initial state of the air, and curve AB represents the cooling of the air in the short initial section of the main. We may assume that the pressure remains constant during this process. The change of state for the remainder of the flow is represented by the isothermal BC between the lines p_1 = const. and p_2 = const. On the Ts-plane the area A_1ABB_1 represents the heat radiated, and the area B_1BCC_1 the heat H generated in overcoming the frictional resistances. For the weight M this heat is given by the usual expression for isothermal expansion

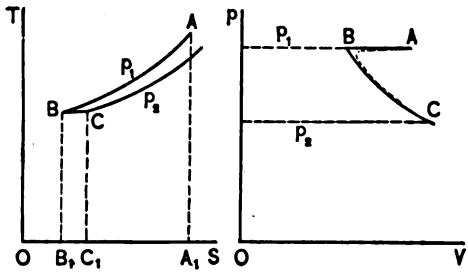


FIG. 47.

$$H = ABMT \log_e \frac{p_1}{p_2}, \tag{1}$$

and the increase of entropy indicated by B_1C_1 is

$$S_2 - S_1 = ABM \log_e \frac{p_1}{p_2}. \tag{2}$$

In the actual process there is, of course, a small drop of pressure during the cooling phase AB, and the curve representing the true change of state will have the form shown by the dash line in the figure.

If the gas has initially the temperature of the surroundings the cooling phase is absent, and the change of state is represented by the isothermal BC alone.

In the case of flowing steam the temperature of the steam remains higher than the temperature of the surroundings and consequently heat is transmitted from steam to air throughout the length of the main. The amount of heat transmitted depends upon the difference of temperature between steam and air, the

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surface exposed to the air, and the time. Let t_s and t_a denote respectively the temperatures of steam and air, A the area in sq. ft. of pipe surface exposed to air, and c the coefficient of transmission; then the heat transmitted per hour is

$$Q = cA(t_s - t_a). \tag{3}$$

Since M denotes the weight of steam flowing per second, the heat given up by one pound of steam is

$$q = \frac{cA(t_s - t_a)}{3600\,M}. \tag{4}$$

The value of the coefficient c depends upon the character of the pipe covering. For bare pipe the value $c = 3.0$ may be taken; for covered pipe $c = 0.35$ to 0.80.

Since the change in velocity between the two ends of the pipe is small, the first fundamental equation ((1) Art. 103) becomes

$$0 = q + i_1 - i_2,$$

in which q denotes the heat *entering* the flowing fluid. If we change the sign of q to denote the heat *leaving* the steam, the equation becomes

$$i_2 = i_1 - q. \tag{5}$$

From the equation of Art. 118, the final pressure p_2 is found, and from (4) and (5) preceding, the thermal potential i_2 may be calculated; hence the final state of the steam may be determined, at least approximately. The following example shows the steps in the calculation.

EXAMPLE. Saturated steam at a pressure of 200 lb. per sq. in. flows in a main 375 ft. long having a nominal diameter of 6 in. $M = 7$ lb. per second. Required the drop in pressure and the final condition of the steam (*a*) for covered pipe, (*b*) with bare pipe.

For a pressure of 200 lb. per sq. in. "extra strong" pipe will be used. The internal diameter is 5.75 in. and the external circumference is 20.81 in. = 1.736 ft.; hence the exposed surface is $1.736 \times 420 = 729$ sq. ft. The coefficient of friction is $0.0072 \times 7^{-\frac{1}{4}} = 0.00545$, and from (2) Art. 118, the loss of pressure is

$$p_1 - p_2 = 174.14 \times 0.00545 \times \frac{7^2 \times 2.292 \times 375}{5.75^5} = 5.05 \text{ lb. per sq. in.}$$

The final pressure may be taken as 195 lb. per sq. in. Taking the coeffi-

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cient of transmission as 3.0 for bare pipe, the heat given up per pound of steam if the outside air is taken at 70° F. is

$$q = \frac{3.0 \times 729 \times (382 - 70)}{7 \times 3600} = 27.1 \text{ B. t. u.}$$

For the covered pipe c may be taken as 0.5; hence for the covered pipe

$$q = 27.1 \times \frac{0.5}{3.0} = 4.5 \text{ B. t. u.}$$

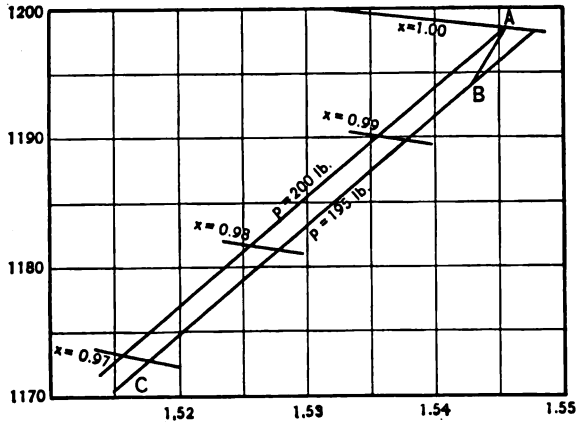


FIG. 48.

In the initial state of the steam $i_1 = 1198.5$ B. t. u.; therefore in the final state

$i_2 = 1198.5 - 4.5 = 1194.0$ for covered pipe
$i_2 = 1198.5 - 27.1 = 1171.4$ for bare pipe

In Fig. 48 the change of state is shown on the Mollier chart. Point A represents the initial state, point B the final state for the covered pipe, and point C the final state when the pipe is bare. The quality indicated by point B is $x = 0.995$, that at point C is $x = 0.968$.

EXERCISES

1. Air is discharged into the atmosphere from a reservoir in which a pressure of 84 lb. per sq. in. is maintained by a compressor. The orifice is circular and has a diameter of 0.28 in. and the temperature of the air in the reservoir is 120° F. Find the weight discharged per minute.

Ans. 6.83 lb.

2. In Ex. 1 let the reservoir pressure be 19.5 lb. per sq. in., the other conditions remaining the same. Find the discharge per minute. Ans. 1.4 lb.

3. Take the pressure in the reservoir as 160 lb. per sq. in., the area of the orifice as 0.43 sq. in. and the temperature as 70° F. Calculate velocity and discharge for back pressures ranging from 160 lb. down to the critica

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pressure, as 150, 140, 130, etc. lb. per sq. in. Plot the results as shown in Figs. 41 and 42.

4. Saturated steam flows through an orifice having an area of 0.27 sq. in. from a boiler in which the pressure is 110 lb. per sq. in. into the atmosphere. Find (*a*) the velocity through the orifice; (*b*) the weight discharged per minute. Ans. (*a*) 1474 ft. per sec.; (*b*) 25.4 lb.

5. Taking the data of Ex. 5 calculate the discharge by the empirical formulas of Napier, Grashof, and Rateau, and compare the results.

6. Steam at a pressure of 165 lb. per sq. in. superheated to 500° F. flows through an orifice having an area of 0.45 sq. in. into a region in which the pressure is 125 lb. per sq. in. Find the weight flowing per hour.

Ans. 3187 lb.

7. With the initial conditions stated in Ex. 6, find the back pressure p_2 at which the discharge attains its maximum value, and find the maximum discharge in pounds per hour.

8. Find the area of an orifice that will discharge 1000 lb. of saturated steam per hour, the initial pressure being 150 lb. per square inch and the back pressure 105 lb. per square inch.

9. In an injector, steam flows through a diverging nozzle into a combining chamber in which a partial vacuum is maintained, due to the condensation of the steam in a jet of water. The initial pressure is 80 lb. per square inch and the pressure in the combining chamber is 8 lb. per square inch. Taking $y = 0.10$ find the velocity of the steam jet at the end of the nozzle.

10. Steam at 160 lb. pressure superheated 100° flows through a nozzle into a turbine cell in which the pressure is 70 lb. per square inch. Find the area of the throat of the nozzle for a discharge of 36 lb. per minute.

Ans. 0.272 sq. in.

11. Find the areas of the throat section and end section of a diverging nozzle for the following conditions. Steam is initially at a pressure of 200 lb. per sq. in. and temperature of 540° F.; it discharges into a turbine cell in which the pressure is 65 lb. per sq. in.; the weight flowing is 2520 lb. per hour; and the value of the coefficient y may be taken as $\frac{1}{8}$.

Ans. (*a*) 0.2644 sq. in.; (*b*) 0.3308 sq. in.

12. Design a de Laval nozzle to discharge 9.5 lb. of steam per minute under the following conditions. The boiler pressure is 85. lb. per sq. in. and the initial quality is 0.982. The steam discharges into a condenser in which the pressure is 6.5 in. of mercury. Take $y = 0.15$.

13. The decrease of exit velocity because of friction is $w_2 - w'_2$ (Art. 106). Show that the ratio $\frac{w_2 - w'_2}{w_2}$ is approximately $\frac{1}{2}y$.

14. Assume several initial steam pressures, calculate the critical pressure p_m and the corresponding acoustic velocity w_m. Show that for steam w_m lies between 1400 and 1800 ft. per sec.

15. Find the diameter of a pipe one mile long to transmit 4400 cu. ft. of free air per minute with an initial pressure of 90 lb. per sq. in. and a drop of pressure not to exceed 8 lb. per sq. in. Ans. 7.88 in.

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16. Compressed air at an initial pressure of 140 lb. per sq. in. is transmitted through a 10-inch main 14,000 feet long. With a drop of pressure of 12 lb. per sq. in., what volume of free air can be transmitted?

Ans. 7800 cu. ft. per min.

17. Work Ex. 16, using Unwin's formula for the coefficient of friction.

Ans. 7593 cu. ft. per min.

18. A pipe 8 inches in diameter and 12,000 feet long transmits 4400 cu. ft. of free air per minute. What initial pressure must be employed to give a pressure of 120 lb. per sq. in. at the end of the pipe? Use (*a*) Fritzche's coefficient and (*b*) Unwin's coefficient and compare results.

Ans. *a*) 131.5 lb.

19. Saturated steam at a pressure of 80 lb. per sq. in. flows through a pipe 6 inches in diameter and 450 feet long. With a drop of pressure of 4.5 lb. per sq. in., what weight of steam is transmitted per hour? Use Unwin's formula for the coefficient ζ. Ans. 15,635 lb.

20. Steam at a pressure of 180 lb. per sq. in. and quality of 0.992 flows through a 5-inch main 450 feet long. Find the drop of pressure for a flow of 285 lb. per minute. Use Fritzche's equation ((4) Art. 118) for ζ. Also use "extra strong" pipe, for which the inside diameter is 4.81 in. and the outside diameter is 5.563 in. Ans. 10.4 lb. per sq. in.

21. Find the quality of the steam at the end of the pipe: (*a*) for bare pipe with $c = 3.0$; (*b*) for covered pipe with $c = 0.6$. Take the external temperature as 60°. Ans. (*a*) 0.954.

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CHAPTER X

THROTTLING PROCESSES

120. Wiredrawing.—The flow of a fluid from a region of higher pressure into a region of much lower pressure through a valve or constricted passage gives rise to the phenomenon known as **wiredrawing** or **throttling.** Examples are seen in the passage of steam through pressure-reducing valves, in the throttling calorimeter, in the passage of ammonia through the expansion valve in a refrigerating machine, and in the flow through ports and valves in the ordinary steam engine. Wiredrawing is evidently an irreversible process, and as such, is always accompanied by a loss of available energy.

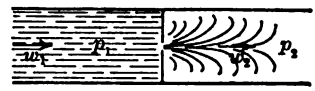


FIG. 49.

The fluid in the region of higher pressure is moving with a velocity w_1, Fig. 49. As it passes through the orifice into the region of lower pressure p_2, the velocity increases to w_2 according to the general equation for flow, namely:

$$\frac{w_2^2}{2g} + Ji_1 = \frac{w_2^2}{2g} + Ji_2. \qquad (1)$$

The increased velocity is not maintained, however, because the energy of the jet is dissipated as the fluid passing through the orifice enters and mixes with the fluid in the second region. Eddies are produced, and the increase of jet energy is returned to the fluid in the form of heat generated through internal friction. Ultimately, the velocity w_2 is sensibly equal to the original velocity w_1; therefore from (1) we obtain

$$i_1 = i_2 \qquad (2)$$

as the general equation of a wiredrawing process. The points representing initial and final states lie, therefore, on a curve of constant thermal potential.

121. Loss due to Throttling.—Let steam in the initial state denoted by point A, Fig. 50, be throttled to a lower pressure,

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the final state being denoted by point B on the constant-i curve AB. Also let T_0 denote the lowest available temperature. The increase of entropy during the change AB is represented by A_1B_1, and this increase multiplied by the lowest available temperature T_0 gives the loss of available energy. Evidently this loss is represented by the area A_1DCB_1

EXAMPLE.—A steam engine is supplied with saturated steam at a pressure of 125 lb. per sq. in. and the pressure of the exhaust is 17 lb. per sq. in. The steam is throttled to a pressure of 85 lb. per sq. in. Required the loss of available energy per pound of steam.

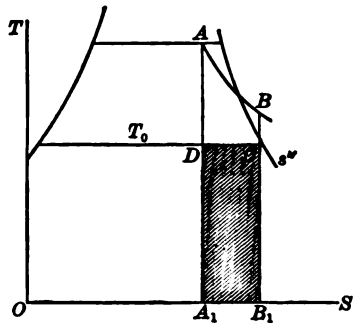


FIG. 50.

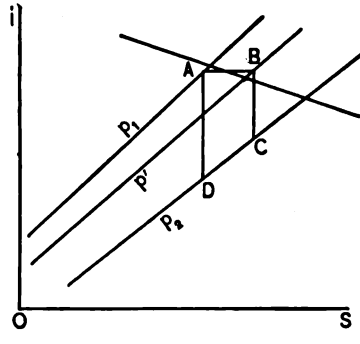


FIG. 51.

For the initial condition $i_1 = 1192.0$ B. t. u. and $s_1 = 1.5858$. The steam is superheated by throttling, and from the table for superheated steam it is found that for $p = 85$ lb. and $i = 1192.0$, the temperature is 328° F., giving a superheat of 11.7°, and the entropy is 1.6260. The increase of entropy is $1.6260 - 1.5858 = 0.0402$, the absolute temperature corresponding to a pressure of 17 lb. is 679, and the loss of available energy is, therefore, $679 \times 0.0402 = 27.32$ B. t. u.

The problem may also be solved by the use of the Mollier chart. Fig. 51 shows on the is-plane the same conditions as are shown in Fig. 50 on the Ts-plane. The line AB represents the throttling from the initial pressure p_1 to an intermediate pressure p'. In both figures AD and BC are adiabatics terminating at the final pressure p_2. The loss of available energy represented by the area A_1DCB_1, Fig. 50, is evidently $i_c - i_d$, and in Fig. 51 this is given by the vertical distance between the points C and D.

Taking the data of the preceding problem, we find from the Mollier chart $i_d = 1044.8$; then passing horizontally from the initial point to the curve

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$p = 85$, and vertically downward to the curve $p = 17$, we find $i_2 = 1072.1$. Hence the loss is $1072.1 - 1044.8 = 27.3$ B. t. u.

122. The Throttling Calorimeter.—An application of the throttling process is seen in the calorimeter devised by Professor Peabody for determining the quality of steam. In the operation of the calorimeter steam from the main is led into a small vessel in which the pressure is maintained at a value slightly above atmospheric pressure. The steam is thus wiredrawn in passing through the valve in the pipe that connects the main and the vessel. For successful operation the amount of moisture in the steam must be small so that, as the result of throttling, the steam in the vessel is superheated.

Let point A, Fig. 50, represent the initial state of the steam; then the point B that represents the state of the steam in the calorimeter lies on a constant-i line through A. From the observed pressure and temperature in the calorimeter the value of i for the second state is found from the table of properties of superheated steam. Having this value of i, the quality x_1 in the initial state is found from the equation

$$i = i_1'' - (1 - x)r_1. \qquad (1)$$

On a Mollier chart the point B may be located from the observed conditions, and point A is then found at the intersection of a horizontal line through B and the line $p_1 = \text{const.}$ (see Fig 51). The quality at A is then read directly from the chart.

EXAMPLE.—The initial pressure of the steam is 140 lb. per sq. in ; the observed pressure in the calorimeter is 17 lb. per sq. in. and the temperature in the calorimeter is 258° F. Required the initial quality.

From the steam table i for 17 lb. and 258° F. is 1173.2. At 140 lb. $i'' = 1193.7$ and $r = 869.6$. Therefore

$$1173.2 = 1193.9 - 869.6(1 - x),$$

whence $1 - x = 0.024$ and $x = 0.976$.

123. The Expansion Valve.—In the compression refrigerating machine the working fluid after compression is condensed and the liquid under the higher pressure p_1 is permitted to flow through the so-called expansion valve into coils in which exists a much lower pressure p_2. Let point A, Fig. 52, on the liquid

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curve represent the initial state of the liquid. The point that represents the final state must lie at the intersection of a constant $-i$ curve through A and line of constant pressure p_2. Evidently we have

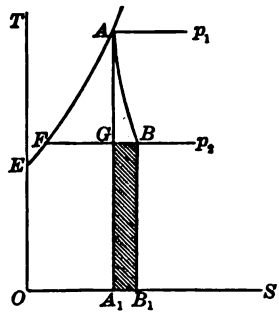


FIG. 52.

$$i_a = i_1',$$

and $$i_b = i_2' + x_2 r_2,$$

where x_2 denotes the quality of the mixture in the final state. Therefore

$$i_1' = i_2' + x_2 r_2, \qquad (1)$$

$$x_2 = \frac{i_1' - i_2'}{r_2}. \qquad (2)$$

The increase of entropy (represented by A_1B_1) is

$$\Delta s = s_2' + \frac{x_2 r_2}{T_2} - s_1', \qquad (3)$$

and the loss of refrigerating effect due to the expansion valve, which is represented by the area A_1GBB_1, is

$$\begin{aligned} T_2 \Delta s &= x_2 r_2 - T_2(s_1' - s_2') \\ &= i_1' - i_2' - T_2(s_1' - s_2'). \end{aligned} \qquad (4)$$

The following equalities between the areas of Fig. 52 are evident:

$$\text{area } OEAA_1 = \text{area } OEFBB_1,$$
$$\text{area } FGA = \text{area } A_1GBB_1.$$

EXAMPLE. Liquid ammonia under a pressure of 175 lb. per sq. in. passes through an expansion valve into a coil in which the pressure is 44 lb. per sq. in. Required the quality of the ammonia in the second state and the loss of refrigerating effect per pound of ammonia.

From the table of the properties of ammonia, the following values are found:

For $p = 175$ lb., $i' = 72.6$, $s' = 0.1190$;
for $p = 44$ lb., $i' = -16.4$, $s' = -0.0341$,
$r = 559.2$, $t = 16.4°$ F., $T = 476$.

Therefore $$x_2 = \frac{62.6 + 16.4}{559.2} = 0.141,$$

and $T_2\Delta s = 62.6 + 16.4 - 476(0.1190 + 0.0341) = 6.12$ B. t. u.

124. Throttling of Gases. Joule-Thomson Effect.—For a perfect gas we have

$$di = c_p dT; \qquad \text{[Art. 68 } (a)\text{]} \qquad (1)$$

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hence the temperature of a perfect gas remains unchanged when the gas is subjected to a throttling process. Actual gases, however, show some change of temperature when throttled.

The classical porous plug experiments of Joule and Lord Kelvin were undertaken for the purpose of estimating the deviation of certain actual gases from the ideal perfect gas. The gases tested were forced through a porous plug and the temperatures on the two sides of the plug were accurately determined. In the case of hydrogen the temperature after passing through the plug was slightly higher than on the high pressure side; air, nitrogen, oxygen, and carbon dioxide showed a drop of temperature.

The ratio of the observed drop in temperature to the drop in pressure, that is, the ratio $\frac{\Delta T}{\Delta p}$, is called the Joule-Thomson coefficient and is denoted by μ. According to the experiments of Joule and Kelvin μ varies inversely as the square of the absolute temperature. That is,

$$\mu = \frac{\alpha}{T_2}. \tag{2}$$

It may be assumed that this relation holds good for air, nitrogen, and other so-called permanent gases within the region of ordinary observation and experiment. At very low temperatures it seems probable that μ varies with the pressure also.

If an expression for the thermal potential i of a gas or vapor is known an expression for μ may be obtained by differentiation. Thus let

$$i = \varphi(T,p) \tag{3}$$

be the given equation; by differentiation we obtain

$$di = \frac{\partial i}{\partial T}\,dT + \frac{\partial i}{\partial p}\,dp. \tag{4}$$

For a throttling process $i =$ const., $di = 0$; hence

$$\left(\frac{\partial T}{\partial p}\right)_{i\,=\,const} = -\frac{\partial i}{\partial p} \Big/ \frac{\partial i}{\partial T}. \tag{5}$$

But

$$\left(\frac{\partial i}{\partial T}\right)_p = c_p$$

therefore

$$\mu = \left(\frac{dT}{dp}\right)_i = -\frac{1}{c_p}\frac{\partial i}{\partial p}. \tag{6}$$

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As an example, take superheated steam, for which

$$i = \alpha T + \tfrac{1}{2}\beta T^2 - \frac{\gamma}{T} - \frac{Am(n+1)}{T^n} p(1 + 2ap^{\frac{1}{2}}) + Acp + i_0. \quad (7)$$

We have

$$\frac{\partial i}{\partial p} = -A\left[\frac{m(n+1)}{T^n}(1 + 3ap^{\frac{1}{2}}) - c\right] \quad (8)$$

and

$$\mu = \frac{A}{c_p}\left[\frac{m(n+1)}{T^n}(1 + 3ap^{\frac{1}{2}}) - c\right]. \quad (9)$$

Comparison of the calculated values obtained from (9) with experimental values affords a test of the accuracy of equation (7).

125. Throttling Curves.—If steam initially dry and saturated be wiredrawn by passing it through a small orifice into a region of lower pressure, then, as has been shown, it will be superheated in its final state. If the lower pressure p_2 is varied, the temperature t_2 will also vary, and the successive values of p_2 and t_2 will be represented by a series of points lying on a curve. By taking various initial pressures a series of such curves may be obtained. Sets of throttling curves for water vapor have been obtained by Grindley, Greissmann, Peake, and Dodge; and for ammonia vapor by Wobsa. The curves deduced from Peake's experiments are shown in Fig. 53. Abscissas represent pressures, ordinates, temperatures. The curves from which the throttling curves start is the curve $t = f(p)$ that represents the relation between the pressure and temperature of saturated steam.

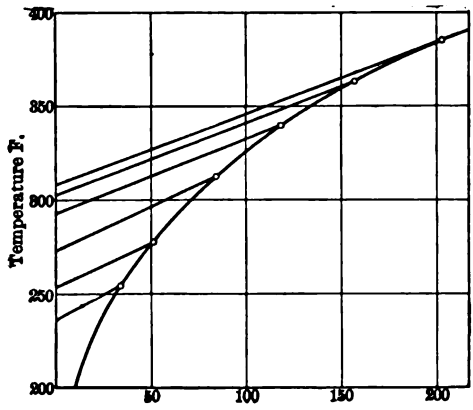


FIG. 53.

The slope of the throttling curve is the derivative $\frac{dT}{dp}$, that is, the Joule-Thomson coefficient μ. For a perfect gas the throttling curves would be horizontal straight lines.

Experiments on throttling have afforded valuable material

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for the investigation of the properties of various substances. Thus with the throttling experiments on steam and the Munich experiments on specific heat of steam, Dr. Davis, was able to deduce a new and accurate formula for the total heat of saturated steam which has replaced Regnault's linear equation.

EXERCISES

1. Steam at a pressure p_1 and quality x_1 is throttled to a pressure p_2. For each case find (*a*) the quality x_2, or the temperature, at the lower pressure; (*b*) the increase of entropy. Check the calculations by the Mollier chart.

	p_1	x_1	p_2
(*a*)	100 lb.	0.98	16 lb.
(*b*)	185 lb.	0.93	35 lb.
(*c*)	75 lb.	0.56	40 lb.
(*d*)	220 lb.	1.00	80 lb.

2. Water is blown from a boiler in which the pressure is 140 lb. per sq. in. This is a throttling process in which the lower pressure is that of the atmosphere. Find the per cent. of the hot water that becomes steam in the process. Ans. 16.7

3. If steam at a pressure of 150 lb. per square inch having a quality of 0.98 is throttled, at what pressure does it become dry saturated steam? Find the increase of entropy.

4. Find the loss of available energy when the pressure of steam is reduced by wiredrawing from 140 to 130 lb. per square inch. The initial quality is 0.98 and back pressure is 5 in. of mercury. Ans. 5.64 B. t. u.

5. In an experiment with a throttling calorimeter the pressure of the steam was 110 lb. per square inch, the pressure in the calorimeter was 16 lb. per square inch, and the temperature of the steam in the calorimeter was 246° F. Required the per cent of moisture in the steam. Ans. 2.5

6. Liquid ammonia under a pressure of 160 lb. per sq. in. is discharged through the expansion valve into the brine coil in which the pressure is 35 lb. per sq. in. Find (*a*) the quality of the mixture entering the coil, and (*b*) the loss of refrigeration per pound of ammonia.

Ans. (*a*) 0.147; (*b*) 6.9 B. t. u.

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CHAPTER XI

THE STEAM ENGINE

126. Cycle Processes.—In any heat motor, heat is conveyed from the source of supply to the motor by some medium, which thus simply acts as a vehicle. In practically all cases the medium is in the liquid or gaseous state, though a motor with a solid medium is easily conceivable. The performance of work is brought about by a change in the specific volume of the medium due to the heat received from the source. By a proper arrangement of working cylinder and movable piston this change of volume is utilized in overcoming external resistances. (In the steam turbine another principle is employed.) The medium must pass through a series of changes of state and return eventually to its initial state, the series of changes thus forming a closed cycle. To use a crude illustration, the medium taking its load of heat from the source at high temperature, delivering that heat to the working cylinder and to the cold body (condenser) and returning to the source for another supply may be compared with an elevator taking freight from an upper story to a lower level and returning empty for another load.

Where the medium is expensive it is used over and over and thus passes through a true closed cycle. Examples are seen in the ammonia refrigerating machine and in the engines and boilers of ocean steamers, in which fresh water must be used. In such cases we may speak of the motor as a **closed** motor. If the medium, on the other hand, is inexpensive or available in large quantities, as air or water, **open** motors are quite generally used. In these the working fluid is discharged into the atmosphere and a fresh supply is taken from the source of supply. Even in this case the medium may pass through a closed cycle, but all the changes of state are not completed in the organs of the motor.

In studying the action of a heat motor, we first investigate the cycle that would represent the various changes of state if all

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the changes proceeded under ideal conditions, that is, without friction, radiation and conduction, wire-drawing, etc. We then attempt to investigate the various modifications of the cycle due to these disturbing influences.

127. Steam Engine Cycles.—The Carnot cycle, having maximum efficiency, would at first appear to be a proper cycle for the steam engine. Three of the four processes are attainable without difficulty: isothermal expansion in the boiler, adiabatic expansion in the cylinder, and isothermal compression in the condenser. The adiabatic compression might be accomplished by a proper arrangement of the organs of the motor; but in practice the isothermal compression is continued until the vapor is entirely

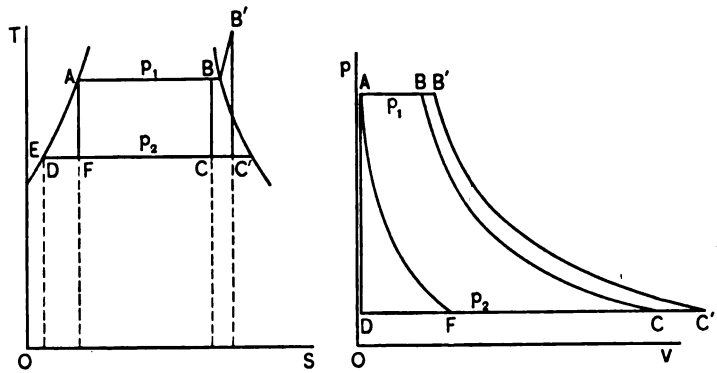


FIG. 54.

condensed and the liquid is then pumped into the boiler at the temperature in the condenser. The resulting cycle is known as the **Rankine cycle.**

In Fig. 54 the Carnot and Rankine cycles are shown on the pv- and Ts-planes. Line AB represents the isothermal expansion in the boiler, and curve BC the adiabatic expansion in the cylinder. Isothermal compression with condensation begins at C. In the case of the Carnot cycle this process is stopped at the state represented by point F and the mixture is compressed adiabatically to the original state A; in the case of the Rankine cycle condensation is continued till the point D on the liquid curve is reached. The liquid is then forced into the boiler as indicated by EA. It should be noted that point D represents the liquid at the tem-

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perature t_2 and pressure p_2 existing in the boiler; point E represents the liquid at the same temperature but under the boiler pressure p_1; and point A represents the liquid at pressure p_1 and at the boiling temperature t_1. On the Ts-plane points D and E are practically coincident: on the pv-plane the segment EA represents the small increase of volume of the liquid due to the heating from t_2 to t_1, therefore points E and A are nearly coincident.

If the fluid is superheated the point B' at the beginning of adiabatic expansion lies in the region of superheat, and curve $B'C'$ represents the adiabatic expansion.

128. Efficiencies of the Cycles.—Fig. 55 shows the Rankine cycle on the is-plane. The segments OB_1, OC_1, OE_1 represent, respectively, the values of the thermal potential i at the points B, C, and E. The changes of state EA and AB proceed under the constant pressure p_1 in the boiler; hence the heat absorbed by the fluid during these processes is equal to the increase of thermal potential. That is

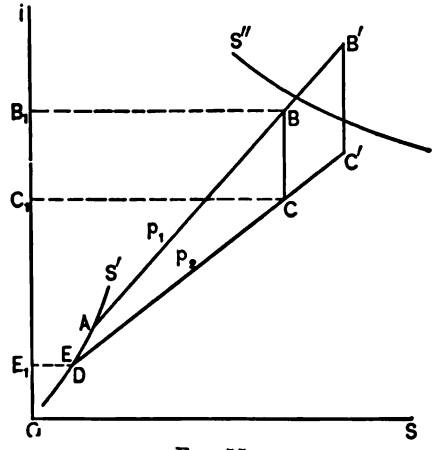


Fig. 55.

$$_eq_b = i_b - i_e, \qquad (1)$$

and this heat is represented by the segment E_1B_1. Similarly the process CD is at the constant pressure p_2, and the heat rejected during this change is

$$_dq_c = i_c - i_d \qquad (2)$$

which is represented by the vertical distance between C and D. Subtracting (2) from (1) we get for (q) the heat transformed into work

$$(q) = {}_eq_b - {}_dq_c = i_b - i_c - (i_e - i_d). \qquad (3)$$

The points D and E are, strictly speaking, not coincident but they may be so assumed without appreciable error. With this assumption, $i_e = i_d$ and

$$(q) = i_b - i_c. \qquad (4)$$

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In the ideal Rankine cycle, therefore, the heat transformed into work is the decrease of thermal potential during adiabatic expansion. In the figure this is represented by the segment $B_1C_1 = BC$.

The efficiency of the cycle is the ratio of (q) to ${}_eq_b$, the heat absorbed; hence

$$\eta = \frac{i_b - i_c}{i_b - i_e}. \tag{5}$$

The three magnitudes i_b, i_c, i_e involved in (1), (4), and (5) are readily determined from given conditions; thus $i_e = i'_2$, the potential of the liquid corresponding to the pressure p_2,

$$i_b = i''_1 - (1 - x_1)r_1,$$

and

$$i_c = i''_2 - (1 - x_2)r_2,$$

where x_1 and x_2 denote the qualities at points B and C respectively. The quality x_1 is known, and x_2 is determined from the adiabatic relation

$$s'_1 + \frac{x_1 r_1}{T_1} = s'_2 + \frac{x_2 r_2}{T_2}.$$

If the initial point, as B', lies in the region of superheat, the initial potential i and entropy s are found directly in the table of superheated steam, and x_2 is readily obtained.

The efficiency of the Carnot cycle $ABCF$, Fig. 54, is

$$\eta = \frac{T_1 - T_2}{T_1}, \tag{6}$$

in which T_1 and T_2 denote the absolute temperatures corresponding to the pressures p_1 and p_2. The heat absorbed during the isothermal expansion AB is x_1r_1, and the heat transformed into work is

$$(q) = x_1 r_1 \frac{T_1 - T_2}{T_1}. \tag{7}$$

The performance of a steam engine is often expressed in terms of the weight of steam required per horsepower hour. Since one horsepower hour is equal to 2546 B. t. u. and the heat transformed into work is (q) B. t. u. per pound of steam, the weight of steam N per horsepower hour is

$$N = \frac{2546}{(q)}. \tag{8}$$

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The heat furnished by the boiler for one horsepower hour may also be used for estimating the performance. Let q_1 denote the heat absorbed by one pound of the fluid; then the heat Q required for one horsepower hour is

$$Q = Nq_1 = \frac{2546}{\eta}. \tag{9}$$

EXAMPLE. Steam is supplied at a pressure of 150 lb. absolute and a quality of 0.98, and the condenser pressure is 4 in. of mercury. Required the efficiencies of the Rankine and Carnot cycles under these conditions.

From the steam table $i'_2 = 93.4$, $i_1 = 1194.7 - 0.02 \times 864.9 = 1177.4$, $s_1 = 1.5704 - 0.02 \times 1.0573 = 1.5493$. The quality x_2 is given by the equation $s_1 = s'_2 + \frac{x_2 r_2}{T_2}$, that is, $1.5493 = 0.1739 + 1.7478x_2$, from which $x_2 = 0.787$. Then $i_2 = 1115.9 - 0.213 \times 1022.5 = 898.1$. For the Rankine cycle the heat absorbed is $i_1 - i'_2 = 1177.4 - 93.4 = 1084.0$ B. t. u., the heat transformed is $i_1 - i_2 = 1177.4 - 898.1 = 279.3$ B. t. u., and the efficiency is therefore $279.3/1084 = 0.258$.

The temperatures corresponding to the two pressures are $t_1 = 358.5°$ F. and $t_2 = 125.4°$ F.; hence the efficiency of the Carnot cycle is

$$\frac{358.5 - 125.4}{358.5 + 459.6} = 0.285.$$

The heat absorbed per pound of steam is $x_1 r_1 = 0.98 \times 864.9 = 847.6$ B. t. u. and the heat transformed into work is $847.6 \times 0.285 = 242.6$ B. t. u. For the Rankine engine the steam consumption per horsepower hour is $2546/279.3 = 9.12$ lb., and for the Carnot engine it is $2546/242.6 = 10.50$ lb. However, the heat required per horsepower hour is:

for the Rankine Engine, $Q = 9.12 \times 1084 = \frac{2546}{0.258} = 9880$ B. t. u.

for the Carnot engine, $Q = 10.50 \times 847.6 = \frac{2546}{0.285} = 8930$ B. t. u.

The ratio of the two efficiencies is $0.258/0.285 = 0.905$.

129. Rankine cycle with Incomplete Expansion.—If the adiabatic expansion is continued until the lower pressure p_2 is attained, as shown in Fig. 56, the volume at the low pressure is very large. Therefore, to reduce the cylinder volume required, the steam is permitted to exhaust from the cylinder at a pressure somewhat higher than the pressure p_2. On the indicator diagram, Fig. 54, *EF* shows the drop in pressure as the steam passes from the cylinder to the condenser. The length *DF* represents the cylinder volume required while the length *DC* represents the cylinder volume required in the case of complete expansion.

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The change of state of the steam in passing from the cylinder to the condenser requires careful consideration. The pressure drops from that indicated by point E, which may be denoted by p_3, to the pressure p_2 in the condenser. The process is essentially a wire-drawing and is therefore irreversible. However, in this case the usual equation for throttling, namely $i_3 = i_2$, is not valid, and a new relation must be deduced.

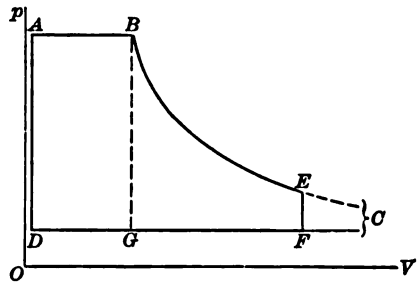


FIG. 56.

Let v_3 denote the volume indicated by point E; without clearance this is the cylinder volume. When the exhaust valve opens the pressure drops from p_3 to p_2 because of the steam leaving cylinder, but the volume of steam remaining is v_3. As the piston moves through its stroke, therefore, work p_2v_3 is done on the steam. The steam in entering the condenser expands to a volume v_2, and in the condenser, therefore, it must do the work p_2v_2 in providing the space it must occupy.

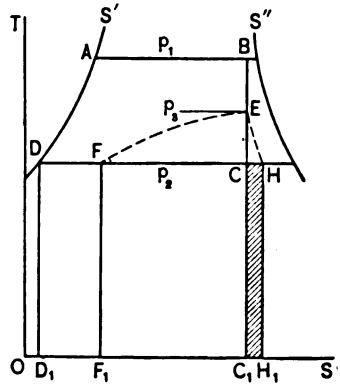


FIG. 57.

The process may be taken as adiabatic. The change of energy is $u_2 - u_3$ and the net work done by the steam is $p_2v_2 - p_2v_3$. Applying the energy equation, we have

$$u_2 - u_3 + A(p_2v_2 - p_2v_3) = 0,$$

or $$u_3 + Ap_2v_3 = u_2 + Ap_2v_2 = i_2. \quad (1)$$

The process just described is shown graphically on the Ts- and is-planes in Fig. 57 and 58. Point E represents the state of the steam at release and point H the state after the passage into the condenser. The point H is determined from the pressure p_2 and the potential i_2 given by (1). The irreversible process is, of course, accompanied by an increase of entropy. With incomplete expansion the segment H_1D_1, Fig. 58, represents the

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heat rejected to the condenser, and the segment B_1H_1 the heat transformed into work. With complete expansion from B to C, segment B_1C_1 represents the heat transformed into work; hence by incomplete expansion the available heat is reduced by the heat represented by segment H_1C_1. This loss is represented on the Ts-plane by the area H_1HCC_1, Fig. 57.

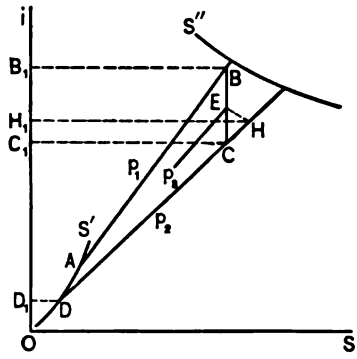


FIG. 58.

Let i_1 denote the thermal potential of the steam at the beginning of adiabatic expansion, that is, in the state represented by point B. Then the heat transformed into work is

$$(q) = i_1 - i_2,$$

and making use of (1),

$$(q) = i_1 - u_2 - Ap_2v_2. \qquad (2)$$

The efficiency of the cycle is

$$\eta = \frac{(q)}{i_1 - i'_2} = \frac{i_1 - u_2 - Ap_2v_2}{i_1 - i'_2}. \qquad (3)$$

EXAMPLE. Taking the data of the example of Art. 128, let the adiabatic expansion be stopped at a pressure of 30 lb. per sq. in. Required the efficiency of the cycle.

The initial entropy is 1.5493, and the quality x_2 after adiabatic expansion to 30 lb. is given by the adiabatic relation $1.5493 = 0.3679 + 1.3340\, x_2$, whence $x_2 = 0.886$. The energy u_2 is $1089.2 - 0.114 \times 870.7 = 989.9$ B. t. u. and the volume v_2 is $0.886 \times 13.76 = 12.19$ cu. ft. The pressure p_2 is 4 in. of mercury which is equal to 1.965 lb. per sq. in., and the product Ap_2v_2, taking p_2 in lb. per sq. *foot*, is $0.1852 \times 1.965 \times 12.19 = 4.4$ B. t. u. The heat transformed is $(q) = 1177.4 - 989.9 - 4.4 = 183.1$ B. t. u.; the heat absorbed is 1084 B. t. u. and the efficiency is $183.1/1084 = 0.169$.

The cycle with incomplete expansion may be subjected to another analysis which is useful in certain deductions. Let it be assumed that the line EF, Fig. 56, represents a change of state, a cooling of the steam at constant volume. The change is shown on the Ts-plane by the curve EF, Fig. 57, and the cycle is closed by FD, which represents condensation at constant pressure. The heat rejected, represented by the area under EFD, is equal to the heat rejected along the path HD; that is, area

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C_1EFDD_1 = area H_1HDD_1, and area CEF = area H_1HCC_1.

It should be emphasized that the path EFD is purely hypothetical and that it is obtained by substituting for the actual process an assumed reversible change of state that gives the same indicator diagram and therefore the same work per pound of steam. The path EHD is the one actually followed.

130. Non-Expansive Cycle.—If the steam is admitted throughout the stroke without cut-off, the adiabatic expansion is lacking, and the indicator diagram is a rectangle, as $ABGD$, Fig. 56. In this case state 3 coincides with state 1, and equation (2) of the preceding article becomes

$$\begin{aligned}(q) &= i_1 - u_1 - Ap_2v_1 \\ &= Ap_1v_1 - Ap_2v_1 \\ &= Av_1(p_1 - p_2). \end{aligned} \qquad (1)$$

131. Effect of Changing the Limiting Pressures.—If the upper pressure p_1 be raised to p'_1 while the lower pressure p_2 is kept the same, the effect is to increase both q_1, the heat absorbed, and (q), the available heat, by an amount represented by the area $AA'B'B$, Fig. 59. Evidently the ideal efficiency is thus increased. If the back pressure p_2 be lowered to p'_2, keeping p_1 the same, the heat q_2 rejected is decreased and the available heat (q) is increased. For the ideal Rankine cycle the increase of available heat would be that represented by the area $D'DCC'$. For the modified cycle with incomplete expansion, however, the increase is represented by the relatively small area $D'DFF'$.

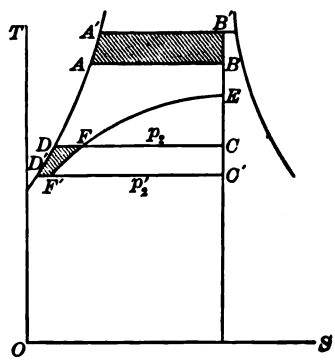


FIG. 59.

It is evident that in the case of the reciprocating steam engine the limitation imposed by the cylinder volume precludes any marked improvement of efficiency from the lowering of the condenser pressure. Herein lies one important advantage of the steam tubine. If properly designed the turbine will discharge

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the necessary volume of steam at the lowest condenser pressures attainable; and nearly the full advantage of the reduced condenser pressure may be utilized.

132. Deviations from the Ideal Cycle.—In the discussion of the ideal Rankine cycle the following conditions are assumed:

1. That the wall of the cylinder and piston are non-conducting, so that the expansion after cut-off is truly adiabatic.

2. Instantaneous action of valves and ample port area so that free expansion or wiredrawing of the steam may not occur.

3. No clearance.

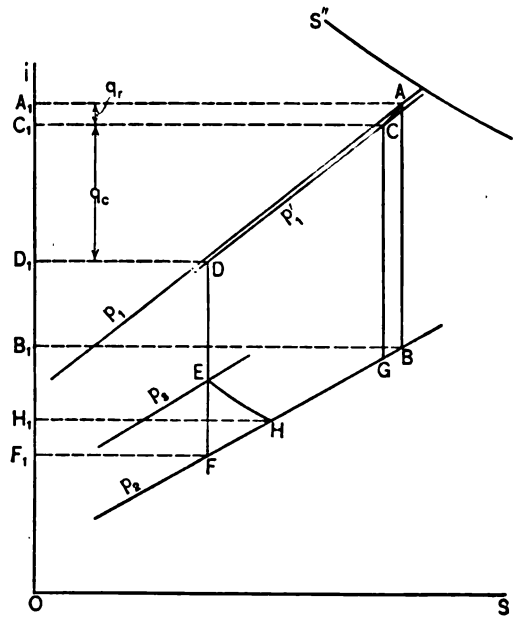


FIG. 60.

In the actual engine none of these conditions is fulfilled. There is a loss of pressure in the steam pipe and a loss of heat to the surroundings. The metal of the cylinder and piston conducts heat and there is, consequently, a more or less active interchange of heat between metal and working fluid, thus making adiabatic expansion impossible. The cylinder must have clearance, and the effect of the cushion steam has to be considered. The valves do not act instantly and a certain amount of wiredrawing is inevitable. It follows that the cycle of the actual engine deviates in many ways from the ideal Rankine cycle, and that the actual efficiency must be considerably less than the ideal efficiency. We may regard the Rankine cycle as an ideal standard unattainable in practice but ap-

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proximated to more and more closely as the imperfections here noted are gradually eliminated or reduced in magnitude.

The effects of some of these imperfections may be shown by diagrams on the *Ts*- and *is*-planes.

(*a*) *Losses in the Steam Pipe.*—Let the point *A*, Fig. 60, represent on the *is*-plane the state of the steam leaving the boiler. The pressure of the steam is p_1 and the thermal potential in this state may be denoted by i. Heat is radiated from the pipe, and there is a drop of pressure from p_1 to p'_1; as a result the state of the steam entering the cylinder is represented by the point *C*. As shown in Art. 119, the decrease of thermal potential between states *A* and *C* is equal to the heat q_r lost by one pound of steam. The loss of effect due to the steam pipe alone may be estimated by a comparison of the segments *AB* and *CG*, the first of which represents the maximum available heat (q), and the second the available heat when the steam expands adiabatically from the initial state *C*.

(*b*) *Loss from Initial Condensation.*—The steam on entering the cylinder comes in contact with metal walls that have been cooled by contact with the low-temperature exhaust steam, and it immediately starts to condense. As the piston moves more of the cylinder wall is exposed and condensation continues; and at cut-off 20 to 50 per cent. of the total weight of the mixture is water. The condensation proceeds under the constant pressure p'_1 and is represented by *CD*, Fig. 60. The heat q_c given up by the mixture is the difference $i_c - i_d$. If now the mixture expands adiabatically to the lower pressure p_2, the segment *DF* ($= i_d - i_f$) gives the heat that may be transformed into work. Comparison of *DF* with *CG* shows the loss due to initial condensation.

(*c*) *Incomplete Expansion.*—If the expansion is stopped at some intermediate pressure p_3 and the mixture is wire-drawn to the pressure p_2, the path *DEH* is followed rather than the path *DF*. The decrease in the heat transformed is $i_h - i_f$, which is represented by the segment F_1H_1.

The effect of the three losses here mentioned is to reduce the heat (q) transformed into work from an amount represented by the segment A_1B_1 to the amount represented by the segment D_1H_1.

(*d*) *Clearance Loss.*—The engine cylinder must be provided

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with a clearance space, the volume of which may vary from two to ten per cent. of the volume swept over by the piston. When steam is admitted to the cylinder it first enters this clearance space, which is filled with the cushion steam at a pressure p'. This pressure depends on the amount of compression and is determined by the setting of the exhaust valve. If the valve is made to close sufficiently early in the stroke the pressure p' may be equal to or even greater than the pressure p_1 of the entering steam. If, as is usual, p' is less than p_1, the entering steam is at first wire-drawn and as a result there is a loss of available energy. The effect of mixing the entering steam with the cushion steam at lower pressure is a slight reduction in quality and thermal potential. This effect would be shown in Fig. 60 by a slight shifting of the point C towards D. Unless the clearance is large and the pressure p' is very small the loss is negligible.

(*e*) *Feed Water at Low Temperature.*— In the preceding discussions it has been assumed that the engine is provided with a condenser. The conditions for a non-condensing engine are shown in Fig. 61. The steam is exhausted into the atmosphere and therefore condenses under atmospheric pressure p_2; the point D represents the state at the end of condensation, that is, water at 212°F. The water then cools to atmospheric temperature, the process being represented by DK, and the state K may be taken as that of the cold feed water pumped into the boiler. Hence KA represents the heating of the water in the boiler. It is seen that the segment KD of the cycle is traversed twice and that the segment K_1D_1 represents additional heat that must be supplied to the boiler without any compensating increase in the available heat. By starting the cycle at point D the heat required to produce the steam may be reduced by the amount $i_d - i_k$. For this purpose a feed water heater is used. The heat rejected in the exhaust is used to heat the

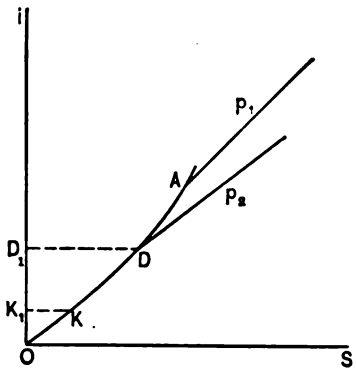


FIG. 61.

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feed water to approximately 212°, the temperature indicated by point D.

133. The Expansion Curve.—It has been assumed that the expansion of the mixture after cut-off is adiabatic. This assumption is, however, never justified by the actual conditions present in the engine cylinder. Before cut-off the incoming steam unless highly superheated is partly condensed, and at the beginning of expansion the mixture, because of the initial condensation, has a quality x_c, which may be as low as 0.50. After expansion begins the condensation generally continues until a point is reached at which the temperature of the steam falls below the temperature of the cylinder wall. For the remainder of the expansion there is, in general, a re-evaporation of the water on the cylinder walls and consequently an increase in the quality of the mixture.

It has been found by experiment that the phenomenon of condensation and re-evaporation is influenced by the initial quality x_c; when this quality is low, 0.5 or 0.6, the re-evaporation is considerable, when it is high, say above 0.85, there is no re-evaporation. Let is be assumed that the pv-equation of the expansion curve is of the form $pv^n = \text{const.}$ Then with re-evaporation, the volume of the mixture is increased at the lower pressures, the curve is more nearly horizontal than it would be if re-evaporation were not present, and consequently the value of n is smaller. It is found that the expansion curves from actual indicater diagrams follow very closely the law $pv^n = \text{const.}$, and that the value of the exponent n is closely related to the quality x_c at cut-off. A low value of x_c gives a low value of n.

. To Mr. J. P. Clayton is due the credit of establishing a definite relation between the variables x_c and n for steam engines working under certain prescribed conditions. Clayton conceived the idea of plotting the indicator diagram on logarithmic cross-section paper. Fig. 62 shows such plots for the head- and crank-end diagrams from a Corliss engine. From the relation

$$pv^n = C \tag{1}$$

we have

$$\log p + n \log v = \log C; \tag{2}$$

therefore when $\log p$ and $\log v$ are plotted, (2) is the equation of

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a straight line. The value of n is given by the slope of this line, that is by the ratio $OX : OY$.

From an examination of a large number of steam-engine indicator diagrams, Clayton established the following facts.

1. The expansion curve is represented closely by the polytropic curve $pv^n = \text{const.}$; that is, the curve when plotted on the logarithmic diagram is practically a straight line. Deviation from a straight line is a sure indication of the leakage of steam past the piston.

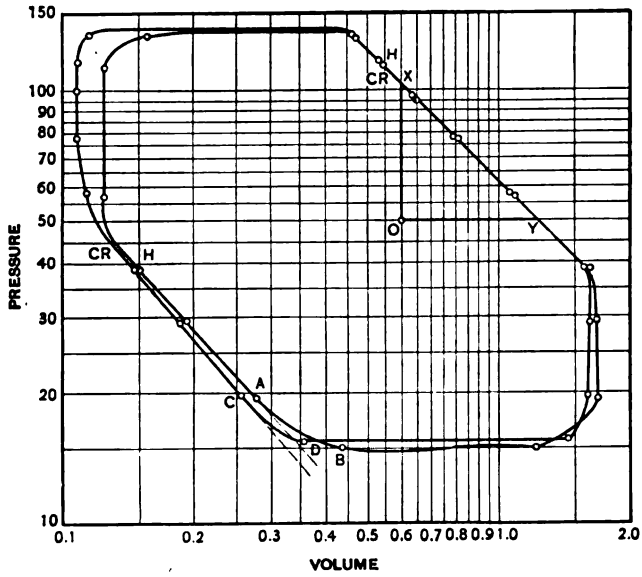


FIG. 62.

2. The value of n may be as low as 0.70 when there is excessive initial condensation and it may be as high as 1.35 when the steam is highly superheated.

3. If the engine is unjacketed and exhausts at a pressure approximately equal to atmospheric pressure, the relation between the exponent n and the quality x_c at cut-off is given by the linear equation

$$x_c = 1.245n - 0.576 \qquad (1)$$

134. Steam Consumption.— Clayton's relation gives a means of calculating with considerable accuracy the steam consump-

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tion of an engine from the data that may be obtained from the indicator diagram. A representative diagram, as shown in Fig. 63, is taken and the various characteristic points, 1, 2, 3, 4 are located, point 1 being the point of cut-off, point 3, the beginning of compression. The distances m and n and the length L of the diagram are measured in any convenient unit. Then if V_c denotes the volume in cubic feet swept through by the piston, the volume V_1 of the contents of the cylinder and clearance space at cut-off is

$$V_1 = V_c \frac{m}{L}, \qquad (1)$$

and similarly the volume V_3 at the beginning of compression is

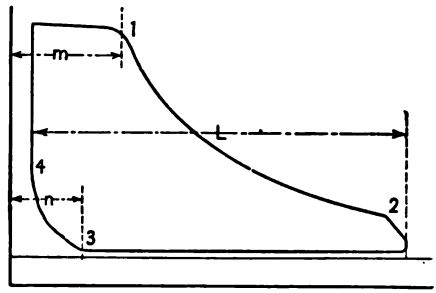


FIG. 63.

$$V_3 = V_c \frac{n}{L}. \qquad (2)$$

Let M denote the weight of steam taken from the boiler per stroke and M' the weight of steam in the clearance space during the compression 3–4. Then at point 1 the volume V_1 is occupied by the weight $M + M'$, and at point 3 the volume V_3 is occupied by the weight M'. If at point 1 the quality is x_c, and the saturation volume corresponding to the pressure p_1 is v''_1, the relation between volume and weight is

$$V_1 = (M + M')x_c v_1'', \qquad (3)$$

and at point 3, likewise

$$V_3 = M'x_3 v_3''. \qquad (4)$$

Combining (3) and (4), we obtain

$$M = \frac{V_1}{x_c v_1''} - \frac{V_3}{x_3 v_3''}. \qquad (5)$$

The values of V_1 and V_3 are given by (1) and (2), and the specific volumes v''_1, v''_3 are found in the steam tables. The value of the exponent n is determined by plotting the indicator diagram on logarithmic cross-section paper, and from this x_c is found from Clayton's relation between x_c and n. It is customary to assume $x_3 = 1$. Having M, the weight of steam per stroke, the

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consumption per horsepower-hour is readily calculated. The result thus calculated will, in general, deviate from the result obtained from a test but the difference should not exceed 4 per cent.

135. Conditions Affecting Cylinder Condensation.—The most serious loss to which the reciprocating steam engine is subject is that due to the interchange of heat between the steam and the metal surfaces of the cylinder. Because of the reciprocating action a fluctuation in the temperature of these surfaces is inevitable. The cylinder walls are in contact alternately with the steam from the boiler at high pressure and temperature and the exhaust steam at much lower temperature; hence the temperature of the inner surface of the wall must vary within these limits, and as the metal is a conductor of heat there must be a continuous interchange of heat between the steam and the metal.

One of the advantages of the steam turbine is the avoidance of alternations of high and low temperature. The steam flows continuously in one direction, and as a result a steady condition is obtained, the metal at any point remaining at practically constant temperature. In the uniflow engine, described subsequently, the fluctuations of temperature are reduced.

The amount of condensation arising from the flow of heat from steam to metal depends upon a number of conditions.

1. *The Expansion Ratio, as Fixed by the Point of Cut-off.*—In theory it is advantageous to have the expansion ratio as large as possible in order to reduce the loss due to incomplete expansion. In a single-cylinder engine, however, an early cut-off accompanied by a large expansion ratio results in excessive initial condensation and a low value of x_c, the quality of the steam at the beginning of expansion. A large part of the heat taken from the incoming steam is used to raise the temperature of the exposed surfaces of the cylinder head, piston, and steam ports, and the heat thus required is the same whether the cut-off is early or late. The point of cut-off, however, determines the weight of steam admitted to the cylinder. With early cut-off the weight of steam is small, and consequently the loss of heat per pound of steam is greater than with late cut-off and a larger weight of steam.

The influence of the point of cut-off on the quality x_c is shown

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by Clayton's experiments on a 12 in. by 24 in. Corliss engine.[1] In one set of experiments with saturated steam at a pressure of 128 lb. per sq. in. absolute the following results were obtained:

Cut-off, per cent of stroke	Quality x_2
7.7	0.540
19.7	0.612
34.4	0.676
46.6	0.697

With steam at a pressure of 127 lb. and superheated to 500° F. the following results were shown

Cut-off	Quality x_2
12.3	0.729
20.5	0.786
32.4	0.907
46.9	0.943

Fig. 64 illustrates the opposing effects of expansion and cylinder condensation. The points A_1, A_2, and A_3 on the line p_1 = const. represent the state of the steam at the beginning of expansion for ½, ¼, and ⅛ cut-off, respectively. Because of the greater condensation, the quality at A_3 is the lowest. At ½ cut-off A_1 B_1 represents the adiabatic expansion and point C_1 the state of the steam at the condenser pressure p_2. The pressure at release (at point B_1) is high and the loss due to incomplete expansion is large. At ⅛ cut-off the loss due to incomplete expansion is much smaller, but because of the low initial quality, the heat transformed into work, represented by segment (q_3), is smaller than at ½ cut-off. It is evident that as the cut-off is is made earlier the loss due to incomplete expansion decreases, that due to condensation increases. At some point the sum of these losses will be a minimum and the engine will show the highest efficiency. Thus in the figure (q_3) the heat available at ¼ cut-off is greater than either (q_1) or (q_2); and at about this cut-off is the point of lowest steam consumption.

2. *Temperature Range.*—The heat absorbed by the metal walls is approximately proportional to the change of the temperature

[1] Bulletin No. 62, Engineering Experiment Station, Univ. of Illinois.

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of the metal; hence the greater the pressure range in the cylinder the greater the initial condensation. In a single cylinder the advantage of a wide pressure range is neutralized to some extent by increased condensation.

3. *Initial Condition of Steam.*—The rate of transfer of heat from a fluid to metal is strongly influenced by the character of the fluid. A gas is a poor conductor of heat and the rate of transfer from gas to metal is smaller than from liquid to metal. If the steam entering the cylinder contains moisture, or even if it is saturated, the water formed by the initial condensation spreads over the metal surfaces and promotes the further transfer of heat; if, on the other hand, the entering steam is superheated sufficiently the rate of transfer between the gaseous medium and metal is retarded and the heat absorbed by the walls is decreased.

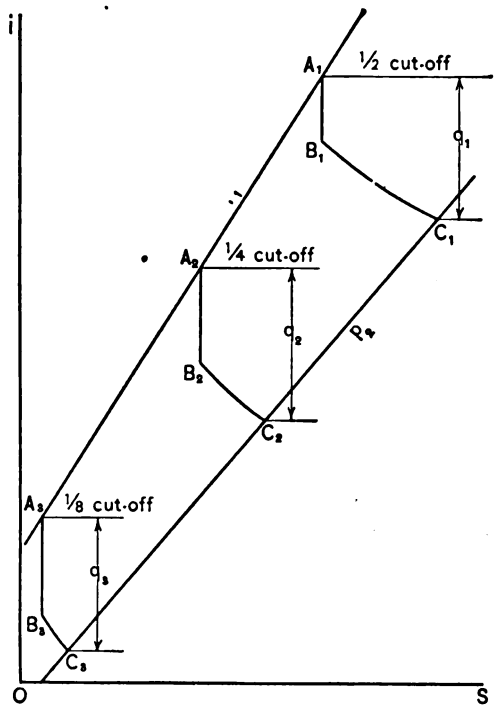


FIG. 64.

4. *Size of Cylinder.*—The weight of steam in the cylinder at given pressure and quality is proportional to cube of a dimension, the surface exposed to steam is proportional to the square of a dimension. Hence the larger the cylinder the greater the weight of steam per unit area of exposed surface, and consequently the less the cylinder condensation. In general, large engines show smaller condensation and higher efficiency than small engines.

5. *Speed.*—Since time is an element in the transfer of heat, it

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may be expected that engines with high rotative speed will show less condensation than slow-speed engines. However, the gain thus effected is neutralized to some extent by increased losses due to wire-drawing and leakage around the valves.

136. Multiple Expansion.—In order to gain the advantages of a wide pressure range and large expansion ratio without the accompanying disadvantage of excessive condensation, multiple expansion is employed. The total pressure range is divided between two, three, or four cylinders; hence in each cylinder the temperature range is correspondingly reduced By the use of multiple expansion, the ratio of final to initial volume may be 10 to 25, whereas in a single cylinder the ratio cannot exceed 4 to 6 without loss of efficiency.

The total loss by condensation in all the cylinders is less than the loss in a single cylinder having the same range of pressure and the same expansion ratio. In the single cylinder the re-evaporation of water during the exhaust stroke is a complete loss; whereas in the case of the compound or triple-expansion engine, the steam produced by re-evaporation in the first cylinder may be utilized in doing work or in heating the walls of the second cylinder, and so on.

The multiplication of cylinders, however, adds to the losses from throttling at the admission and exhaust ports and external radiation from the cylinders, receivers, and piping. As a rule, compounding gives increased economy for pressures above about 100 lb.; for pressures ranging from 175 to 225 lb. triple-expansion engines are used.

In addition to superior economy, multiple expansion engines have certain mechanical advantages. The large low-pressure cylinder is designed to carry only a fraction of the boiler pressure, and the high-pressure cylinder which must withstand the full boiler pressure has a relatively small diameter. With the receiver type of engine the cranks may be set at any desired angles, and as a result the turning effect on the shaft is more uniform than with a single cylinder.

137. Steam Jackets.—In certain types of steam engines the steam jacket is used to reduce cylinder condensation. The cylinder is constructed with an annular space around it and this space is filled with steam from the boiler. Frequently the

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cylinder heads are also jacketed. The flow of heat from the jacket steam keeps the cylinder walls at a higher temperature during expansion and exhaust and thereby reduces the temperature variation. As a result, the initial condensation is decreased, the condensation being transferred from the steam in the cylinder to the steam in the jacket. The heat supplied by the jacket during expansion increases the work of expansion but since there is a drop of temperature through the wall and the film of water on the inner surface, the efficiency with which this heat is utilized is low. The heat supplied by the jacket during exhaust is carried by the exhaust steam directly into the condenser and has no other effect than to increase the burden on the condenser. In the case of a compound engine, however, some of the heat thus thrown into the exhaust of the high pressure cylinder may be utilized in the low-pressure cylinder.

If the gain from the reduction of condensation exceeds the direct losses, an increase of economy will result from the use of steam jackets. From a comparison of numerous tests Professor Peabody draws the conclusion "that about ten per cent. can be gained by using steam-jackets on simple and compound engines and that fifteen per cent. can be gained by their use on triple-expansion engines; provided that these conclusion shall not be applied to engines of more than 300 horsepower. The saving on massive engines of 1000 horsepower or more is likely to be smaller, and very large engines may derive no benefit from steam jackets. On the other hand, a saving of 25 per cent. may be obtained from jackets on small engines of five or ten horsepower."

138. Superheating.—The most effective means of reducing cylinder condensation is the use of superheated steam. As the steam comes in contact with the colder metal surfaces heat passes from the steam to the metal but no water is formed until so much heat is removed as will reduce the steam to the state of saturation. The rate of transfer between the gas and the metal is much slower than it is when water is present; and if the steam is sufficiently superheated, initial condensation may be obviated and the steam may be dry at the beginning of expansion. The influence of superheat on the quality x_c at cut-off is shown by Clayton's experiments on a 12 in. by 24 in. Corliss engine. Tests

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were made with saturated steam and also with steam superheated to 500° F. Some of the results are shown in the following table.

Number of test	Absolute press., lb. per sq. in.	Cut-off, per cent. of stroke	Quality at cut-off	Condition of steam
4	70.3	41.2	0.606	Saturated
43	72.3	41.3	0.859	Superheated
9	89.5	42.6	0.629	Saturated
47	90.5	41.5	0.822	Superheated
18	108.9	25.4	0.588	Saturated
50	110.0	22.3	0.838	Superheated
34	128.5	23.2	0.537	Saturated
68	126.8	23.1	0.700	Superheated
39	127.9	46.0	0.697	Saturated
74	127.1	46.9	0.943	Superheated

From these tests it appears that an increase of 0.01 in the quality x_c requires from 6.5 to 9.5 degrees of superheat. If 8° F. be taken as a mean value, then to increase x_c from 0.60 to 1.00 would require $8 \times 40 = 320$ degrees of superheat.

The heat required to superheat the steam must, of course, be added to the heat required to produce saturated steam; but by the addition of 15 to 20 per cent. to the expense, the receipt in the form of work may be increased perhaps 30 or 40 per cent. Experiments indicate that by the use of steam superheated to 600° F., the saving may be as high as 20 per cent. for simple engines, 16 per cent. for compound engines, and 8 per cent. for triple-expansion engines.[1]

139. The Uniflow Engine.—A large part of the ill effect due to the reciprocating motion of the steam engine and the consequent alternation of hot and cold cylinder walls is obviated in the **uniflow** or **straightflow** engine. As shown in Fig. 65, the piston has a length nearly equal to one-half the length of the stroke. The exhaust ports are placed in the middle of the cylinder barrel,

[1] Marks, Mechanical Engineers Handbook, p. 953.

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and exhaust occurs when the piston uncovers these ports, which is at about nine-tenths of the stroke. The exhaust port area is large and the pressure drops rapidly when the ports are opened. On the return stroke compression begins as soon as the exhaust ports are closed and the clearance is so chosen that the pressure at the end of compression is nearly or quite equal to the boiler pressure. Most of the water formed during the expansion is swept out in the exhaust, and the nearly dry steam left in the

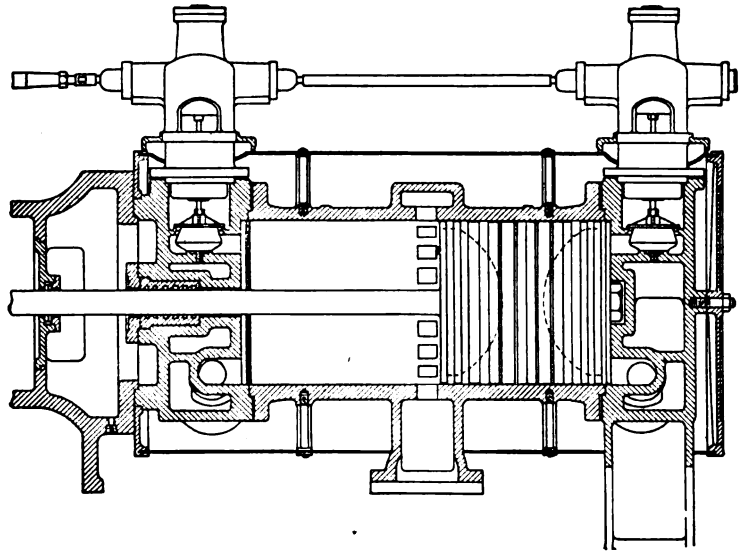


FIG. 65.

cylinder is superheated by the compression. The steam entering from the boiler comes in contact with surfaces at a temperature higher than its own temperature, consequently there can be no initial condensation.

The uniflow engine approximates to the condition of steady temperature found in the steam turbine. While there is a variation of temperature during the revolution, it is much smaller than in the ordinary type of steam engine. The cylinder heads are kept permanently at a high temperature, the center of the cylinder barrel at the ring of exhaust ports is at a lower temperature. By the interposition of the piston the entering steam is kept from contact with the cold part of the cylinder.

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Tests of uniflow engines show excellent economy. A simple condensing uniflow engine has about the same economy as the best compound engine. Furthermore, the economy is nearly constant for wide variations of load.

140. Regulation by Throttling.—The regulation of small steam-engines is sometimes effected by wire-drawing the entering steam to a lower pressure as the load decreases. The cut-off remains the same. If the ideal conditions of the Rankine cycle are assumed, it is easily shown that regulation by throttling is wasteful and inefficient; if, on the other hand, actual conditions are taken into account, the waste is not so apparent. The following example illustrates this statement.

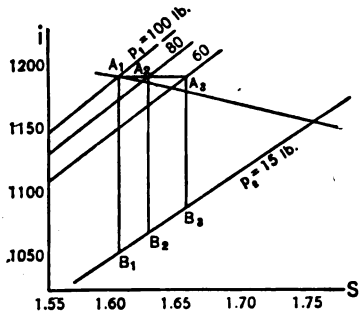


FIG. 66.

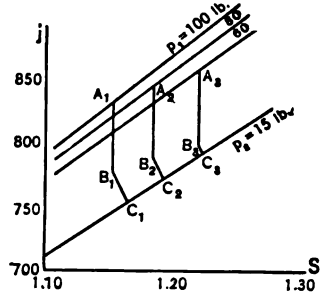


FIG. 67.

Let the boiler pressure be 100 lb. absolute, the exhaust pressure 15 lb., and let the steam originally saturated be throttled to 80lb. and 60 lb. Fig. 66 shows the changes of state under ideal conditions. The initial state of the steam is represented by point A_1 on the saturation curve, and A_1B_1 represents the adiabatic expansion to $p_2 = 15$ lb. The throttling to 80 lb. is represented by the constant-i line A_1A_2, and A_2B_2 represents the adiabatic expansion to 15 lb. Similarly $A_1A_3B_3$ represents the throttling to 60 lb. and the subsequent expansion. For the three cases the heat transformed into work is

p = 100 lb., A_1B_1 = 1188.4 − 1049.4 = 139.0 B. t. u.
p = 80 lb., A_2B_2 = 1188.4 − 1065.2 = 123.2 B. t. u.
p = 60 lb., A_3B_3 = 1188.4 − 1085.6 = 102.8 B. t. u.

The three numbers are proportional to 1 : 0.886 : 0.740; that is, throttling to 60 lb. apparently gives a loss of 26 per cent.

Fig. 67 shows what happens when the actual conditions are represented approximately. Point A_1 represents the condition of the steam at cut off and after initial condensation. The quality x_c is taken as 0.60. The

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throttling of the steam superheats it slightly and thereby reduces somewhat the cylinder condensation; hence the qualities at A_2 and A_3 are taken arbitrarily as 0.625 and 0.65. The cut off is the same in the three cases, and taking the expansion ratio as $3\frac{1}{3}$, the pressures at the end of expansion are approximately 30, 24, and 18 lb., as indicated by points B_1, B_2, B_3. The points C_1, C_2, C_3 are located on the line $p_2 = 15$ lb. by the aid of Eq. (1), Art. 129. The available heat in each case is given by the vertical distance between points A and C.

For 100 lb., $(q) = 79.4$ B. t. u.
80 lb., $(q) = 75.6$ B. t. u.
60 lb., $(q) = 70.6$ B. t. u.

These numbers are proportional to 1 : 0.952 : 0.889. Hence the loss by throttling to 60 lb. is only 11 per cent. instead of 26 per cent.

Experiments indicate that the curve of efficiency with varying load is about the same for regulation by throttling as for regulation by changing the point of cut-off. This statement applies to small single-cylinder engines.

141. Efficiency Standards.—The performance of a steam engine may be measured by three standards. 1. By the efficiency, based on either the heat supplied or the heat available. 2. By the weight of steam used per horsepower-hour. 3. By the heat consumed per horsepower-hour, or per horsepower-minute.

By the efficiency of an engine is meant the ratio of the output of work to the energy supplied from external sources. In the case of the steam engine (and also the steam turbine) there are several possible interpretations of the term.

Let q = heat per pound of steam supplied to the engine.
(q) = heat per pound of steam transformed into work.
$(q)_R$ = heat per pound of steam transformed into work by an engine working in an ideal Rankine cycle.

The ratio $\eta_1 = \dfrac{(q)}{q}$ is the thermal efficiency of the engine, and likewise the ratio $n_R = \dfrac{(q)_R}{q}$ is the thermal efficiency of the ideal Rankine engine operating under the same conditions. Of the heat q supplied the part $(q)_R$ may be considered the *available heat*, that is, the maximum quantity of heat that can be transformed under the conditions by an engine having no superfections. The remaining heat, $q - (q)_R$, is under any circumstances

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unavailable. If now the engine is changed with only the available heat, its efficiency is given by

$$\eta_2 = \frac{(q)}{(q)_R} = \frac{\eta_1}{\eta_R}. \tag{1}$$

This efficiency has been called the *potential efficiency*, and by Greene the *practical efficiency*. It is clear that the efficiency n_2 rather than the thermal efficiency n_1 is the useful criterion of the performance of an engine.

Let W denote the work shown by the indicator diagram, the equivalent of the heat (q) transformed; thus

$$W = J(q), \text{ or } (q) = AW;$$

and let W_b denote the work delivered at the brake. Then the ratio

$$\eta_3 = \frac{W_b}{W} = \frac{AW_b}{(q)} \tag{2}$$

is the *mechanical efficiency* of the engine.

The product

$$\eta_1 = \eta_R \cdot \eta_2 \cdot \eta_3 = \frac{(q)_R}{q} \cdot \frac{(q)}{(q)_R} \cdot \frac{AW_b}{(q)} = \frac{AW_b}{q} \tag{3}$$

is the ratio of the net work obtained to the heat supplied, and it may be designated the *overall efficiency* of the engine. The efficiency η_R depends upon the pressures and temperatures employed; it will be largest for condensing engines using high boiler pressures and superheated steam. The efficiency n_2 is improved by superheating, jacketing, compounding, and other devices to reduce thermal losses. And the efficiency n_3 depends on the mechanical construction of the engine.

As shown in Art. 128, the steam consumption of an engine per horsepower-hour is given by the formula

$$N = \frac{2546}{(q)}. \tag{4}$$

For the ideal Rankine engine,

$$N_R = \frac{2546}{(q)_R}; \tag{5}$$

hence the efficiency n_2 is given by the ratio

$$\eta_2 = \frac{(q)}{(q)_R} = \frac{N_R}{N}. \tag{6}$$

In these equations N denotes the steam used in the cylinder.

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If steam jackets are used the steam supplied to the jackets must be added, and in this case equation (6) is not valid.

While the steam consumption is often used in reporting the performance of a steam engine, it gives an unsatisfactory basis for the comparison of engines working under different conditions.

Engine performance may be estimated in terms of the heat required from the source for one indicated horsepower-hour or horsepower-minute.

$$1 \text{ h.p-hr.} = 2546 \text{ B. t. u.}$$
$$1 \text{ h.p.-min.} = 42.44 \text{ B. t. u.}$$

Since of the heat q received from the source only the heat (q) is transformed into work, the heat Q required from the source to give 1 h.p.-hr. is

$$Q = 2546 \frac{q}{(q)} = \frac{2546}{\eta_1}, \tag{7}$$

and the heat Q' required for 1 h.p.-min. is

$$Q' = \frac{42.44}{\eta_1}. \tag{8}$$

The method of stating engine performance in terms of thermal units per horsepower-hour is advantageous in the comparison of various kinds of heat engines, as steam engines and internal combustion engines; also in comparisons to establish the advantages of jacketing, compounding, or superheating.

The following example, the data for which were taken from Peabody's Thermodynamics, illustrates the application of the various efficiency standards.

In an engine test the steam was furnished at a pressure of 157.7 lb. per sq. in. and quality 0.988, and the back pressure was 4.5 lb. per sq. in. The weight of steam per h.p.-hr. was 13.73 lb., of which the weight supplied to the cylinder was 10.86 lb. and the weight condensed in the jackets 2.87 lb.

The heat supplied per pound of steam admitted to the cylinders was $i_1'' - (1 - x_1)r_1 - i_2' = 1195.5 - 0.012 \times 861.5 - 126 = 1059.2$ B. t. u.; and the heat supplied per pound of steam admitted to the jackets was

$$x_1 r_1 = 0.988 \times 861.5 = 851.2 \text{ B. t. u.}$$

Hence the heat supplied per h.p.-hr. was

$$1059.2 \times 13.73 + 851.2 \times 2.87 = 13{,}943 \text{ B. t. u.}$$

The heat supplied per h.p.-min. was $13943 \div 60 = 232.4$ B. t. u. From (7) or (8) the efficiency of the engine was

$$\eta_1 = \frac{2546}{13943} = \frac{42.44}{232.4} = 0.1826$$

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For the Rankine cycle under the conditions of operation, we find

$$i_1 = 1185.2, \qquad x_2 = 0.815, \qquad i_2 = 944.7$$

$$(q)_R = 1185.2 - 944.7 = 240.5 \text{ B. t. u.}$$

$$\eta_R = \frac{240.5}{1185.2 - 126} = 0.227.$$

Therefore the ratio of the efficiencies is

$$\eta_2 = \frac{\eta_1}{\eta_R} = \frac{0.1826}{0.227} = 0.804.$$

For the ideal Rankine cycle the steam consumption would be

$$N_R = \frac{2546}{(q)_R} = \frac{2546}{240.5} = 10.59 \text{ lb. per h.p.-hr.}$$

The ratio of 10.59 lb. to the actual steam consumption 13.73 lb. is $10.59 \div 13.73 = 0.771$, which is not at all in agreement with the true value of η_2, *i.e.*, 0.804.

EXERCISES

1. A steam engine operates in an ideal Rankine cycle under the conditions following

	p_1	x_1 (or t_1)	p_2
(*a*)	105 lb.	0.98	17 lb.
(*b*)	120 lb.	0.98	5 in. of mercury
(*c*)	160 lb.	1.00	16 lb.
(*d*)	220 lb.	560° F.	2.5 in. of mercury

In each case find (1) heat transformed into work per pound of steam; (2) the efficiency.

2. In examples 1(*b*) and 1(*d*) find the heat transformed into work and the efficiency if the Carnot cycle is used.

3. In the same examples find the heat furnished by the boiler per horse-power-hour for (*a*) Rankine cycle, (*b*) Carnot cycle.

4. Let the pressure p_2 be fixed at 5 in. of mercury. Take $x_1 = 1.00$, assume various boiler pressures, as $p_1 = 80$, 100, 120, etc., lb. per sq. in. Calculate the efficiency of the Rankine cycle, and plot a curve showing the relation between η and p_1.

5. Find the efficiency of a Rankine cycle with incomplete expansion under the following conditions. $p_1 = 90$ lb., $x_1 = 0.97$, $p_2 = 16$ lb. At the end of adiabatic expansion $p_3 = 40$ lb. Find also the quality of the steam after its passage through the exhaust port.

6. In a cycle with incomplete expansion the steam at release has a pressure of 22 lb. per sq. in. and a quality 0.88. The condenser pressure p_2 is 5 in. of mercury. Find the potential i_2 and quality x_2 of the steam after entering the condenser. Find the heat abstracted per pound during condensation.

7. Steam is supplied at a pressure of 190 lb. per sq. in. superheated to 480° F., and the condenser pressure is 4 in. of mercury. Find the increase of the efficiency obtained by reducing the back pressure to 2 in. of mercury, assuming that the ideal Rankine cycle is followed.

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8. Find the increase of efficiency obtained by this reduction of back pressure in the case of the incomplete Rankine cycle with 24 lb. per sq. in. as the pressure p_2 at release.

9. In an engine test the following data were obtained. Boiler pressure 152.5 lb. per sq. in. gauge; initial quality, 1.00; condenser pressure 3.9 in. of mercury; steam consumption per i.h.p.-hr. 15.0 lb. Unjacketed cylinders. Find the efficiencies η_1 and η_2 and the heat supplied per i.h.p.-min.

10. The following values of the heat consumed per i.h.p.-min. in the best performances of reciprocating steam engines using superheated steam are given in the Mechanical Engineers' Handbook, p. 962.

Simple non-condensing	300 B. t. u.
Simple condensing	226 B. t. u.
Compound non-condensing	245 B. t. u.
Compound condensing	200 B. t. u.
Triple condensing	190 B. t. u.
Quadruple condensing	169 B. t. u.

Find the corresponding values of the thermal efficiency η_1.

11. A steam consumption of 9.9 lb. per i.h.p.-hr. is reported for a Stumpf uniflow engine using steam at a pressure of 162 lb. per sq. in. and a temperature of 518° F. Taking the condenser pressure as 4 in. of mercury, what is the efficiency η_2 shown by this test?

12. A jacketed non-condensing engine is supplied with saturated steam at a pressure of 120 lb. and the back pressure is 16 lb. per sq. in. The total weight of steam used is 20.5 lb. per i.h.p.-hr. of which 17.6 lb. passes through the cylinder and 2.9 lb. is condensed in the jacket and the water is returned to the boiler. The feed water enters the boiler at a temperature of 190° F. Find the heat required per i.h.p.-min., and the efficiencies η_1 and η_2.

Ans. 345.7 B. t. u., $\eta_1 = 0.123$, $\eta_2 = 0.802$.

13. The following data, given in the Mechanical Engineers Handbook, apply to the ideal Rankine cycle with incomplete expansion. Check several of these results.

Ratio of Expansion	Saturated steam. Back pressure, 2 lb. per sq. in.			
	Steam pressure lb. per sq. in.	B. t. u. per i.h.p.-min.	Steam consumption, lb. per i.h.p.-hr.	Efficiency η_1
5	100	241	13.2	0.176
	130	234	12.8	0.180
	160	230	12.5	0.182
15	100	191	10.5	0.222
	130	186	10.1	0.230
	160	181	9.9	0.234
	215	176	9.6	0.240

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14. From the steam table take various pressures from 120 lb. to 15 lb. per sq. in. and the corresponding values of v_1'' the volume per pound of saturated steam. Plot the points on the pv-plane, and show that the pv-curve is given approximately by the equation $pv^{1.066} = \text{const.}$ Find the external work done when 1 lb. of steam expands from 120 lb. to 15 lb. along this "dry steam" curve.

15. Steam at a pressure of 108 lb. and quality 0.98 is supplied to an engine, but it is throttled to a pressure of 91 lb. before reaching the cylinder. The back pressure is 17 lb. Assuming that there are no other losses, what is the decrease in efficiency due to throttling?

REFERENCES

PEABODY: Thermodynamics of the Steam Engine, Chap. VIII, XI, XII.
MARKS: Mechanical Engineers' Handbook, 949–964.
GREENE: Heat Engineering, Chap. V, VI.
CLAYTON: Bulletin No. 58, Engineering Experiment Station, Univ. of Illinois.
HECK: The Steam Engine.
BERRY: Temperature Entropy Diagram, Chap. XI, XIV.

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CHAPTER XII

THE STEAM TURBINE

142. Comparison of the Steam Turbine and Reciprocating Engine.—The essential distinction between the two types of vapor motors—turbines and reciprocating engines—lies in the method of utilizing the available energy of the working fluid. In the reciprocating engine this energy is at once utilized in doing work on a moving piston; in the turbine there is an intermediate transformation, the available energy being first transformed into the energy of a moving jet or stream, which is then utilized in producing motion in the rotating element of the motor.

While the turbine suffers from the disadvantage of an added energy transformation with its accompanying loss of efficiency, it has a compensating advantage mechanically. With any motor the work must finally appear in the rotation of a shaft; hence, intermediate mechanism must be employed to transform the reciprocating motion of the piston to the rotation required. Evidently this is not the case with the turbine, which is thus from the point of view of kinematics a much more simple machine than the reciprocating engine. Many unsuccessful attempts have been made to construct a motor (so-called rotary engine) in which both the intermediate mechanism of the reciprocating engine and the intermediate energy transformation of the turbine should be obviated.

With ideal conditions it is easily shown that the two methods of working produce the same available work and, therefore, give the same efficiency with the same initial and final conditions. Thus the Rankine ideal cycle gives the maximum available work per pound of steam of a reciprocating engine with the pressures p_1 and p_2. It likewise gives (Art. 106) the kinetic energy per pound of steam of a jet flowing without friction from a region in which the pressure is p_1 into a region in which it is p_2. Hence if this kinetic energy is wholly transformed into

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work, the work of the turbine per unit weight of fluid is precisely equal to that of the reciprocating engine. Under ideal conditions, therefore, neither type of motor has an advantage over the other in point of efficiency.

Under actual conditions, however, there may be a considerable difference between the efficiencies of the two types. Each type has imperfections and losses peculiar to itself. The reciprocating engine has losses from cylinder condensation; the turbine, from leakage and from friction between the moving fluid and the passages through which it flows. It is a question which set of losses may be most reduced by careful design.

Aside from the question of economy, the turbine has certain advantages over the reciprocating engine in the matters of weight, cost, and durability (associated with certain disadvantages), and these have been sufficient to bring about the use of turbines rather than reciprocating engines in many modern power plants and also in marine service.

143. Classification of Steam Turbines.—Steam turbines may be divided broadly into two classes in some degree analogous to the impulse water wheel and the water turbine, respectively. In the first class, of which the de Laval turbine may be taken as typical, steam expands in a nozzle until the pressure reaches the pressure of the region in which the turbine wheel rotates. The jet issuing from the nozzle is then directed against the buckets of the turbine wheel, Fig. 68, and the impulse of the jet produces rotation. It will be noted that with this type of turbine only a part of the buckets are filled with steam at any instant, even if several nozzles are used.

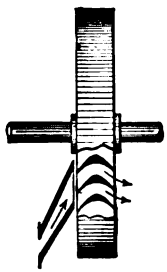


FIG. 68.

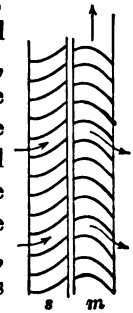


FIG. 69.

In turbines of the second class, the steam flows through guide vanes in a stationary ring s, Fig. 69, and then through blades in the circumference of the moving wheel m. The guides and wheels "run full," that is, the stationary and moving blades are filled with steam throughout the entire circumference. The pressure of the steam is reduced during the passage through

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the blades both in the guide and turbine wheels. In the turbine of the first type all the available internal energy of the steam is transformed into kinetic energy of motion before the steam enters the turbine wheel, while in the turbine of the second type part of the internal energy is transformed into work during the passage of the fluid through the wheel.

The terms *impulse* and *reaction* have been used to designate turbines of the first and second class, respectively. Since, however, both impulse and reaction are present in each type, these terms are somewhat misleading, and the more suitable terms *velocity* and *pressure* have been proposed. Thus a de Laval turbine is a velocity turbine; a Parsons turbine is a pressure turbine.

The principal characteristics of the two classes are:

Velocity turbine	Pressure turbine
1. Only partly filled with steam.	1. Runs full.
2. Pressure drops in nozzles, remains constant in blades.	2. Pressure drops continuously through guides and blades.
3. High steam velocities.	3. Relatively low steam velocities.
4. Blades may be symmetrical.	4. Blades necessarily unsymmetrical.

144. Work of a Jet.—While the problems relating to the impulse and reaction of fluid jets belong to hydraulics, it is desirable to introduce here a brief discussion of the general case of the impulse of a jet on a moving vane.

Let the curved blade have the velocity c in the direction indicated, Fig. 70, and let w_1 denote the velocity of a jet directed against the blade. The velocity w_1 is resolved into two components, one equal to c, the velocity of the blade, the other, therefore, the velocity a_1 of the jet relative to the blade. The angle of the blade and the velocity c should be so adjusted that the direction of a_1 is tangent to the edge of the blade at entrance. The jet leaves the blade with a relative velocity a_2 which may be greater than or less than the entrance velocity a_1. If there is a drop of pressure as the steam passes through the blades, a_2 will exceed a_1; if there is no drop of pressure a_2 will be less than a_1 on

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account of friction. The velocity a_2 combined with the velocity c of the blade gives the absolute exit velocity w_2. It is convenient to draw all the velocities from one point O as shown in the velocity diagram.

The absolute entrance and exit velocities w_1 and w_2 may be resolved into components w_1' and w_2' in the direction of the motion of the vane and w_1'' and w_2'' at right angles to this direction, that is, parallel to the axis of the wheel that carries the vane. These latter may be termed the *axial* components, the former the *peripheral* components. The driving impulse of the jet depends upon the change in the peripheral component only. To deduce an expression for the impulse we proceed as follows.

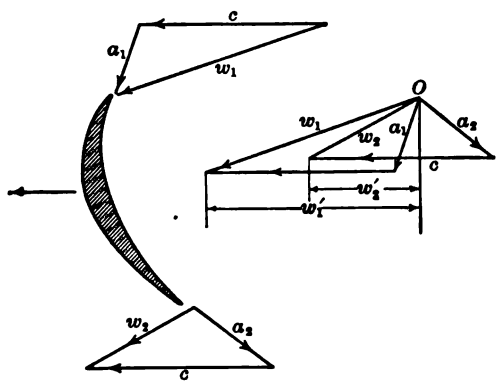


FIG. 70.

Let Δm denote the mass of fluid flowing past a given cross section in the time Δt; then the stream of fluid in contact with the blade may be considered as made up of a number of mass elements Δm, and in the time element Δt one mass element enters the vane with a peripheral velocity w_1' and another leaves it with a peripheral velocity w_2'. The effect is the same as if a single element Δm by contact with the blade had its velocity decreased from w_1' to w_2' in the time Δt. From the fundamental principle of mechanics, the force required to produce the acceleration $\frac{w_2' - w_1'}{\Delta t}$ is

$$p = \Delta m \frac{w_2' - w_1'}{\Delta t}. \qquad (1)$$

This force is the force exerted by the blade upon the element Δm; an equal and opposite force is, therefore, the impulse of Δm on the vane.

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If M denotes the weight of steam flowing per second, then $\Delta m = \frac{M}{g}\Delta t$, and we have for the force exerted by the jet on the vane in the direction of the velocity c

$$p = \frac{M}{g}(w_1' - w_2'). \tag{2}$$

Evidently this equation holds equally well when the weight M flowing from the nozzle is divided among several moving vanes.

The product pc of the peripheral force and peripheral velocity of vane gives the work per second; therefore,

$$\text{work per second} = \frac{Mc}{g}(w_1' - w_2'), \tag{3}$$

and

$$\text{work per pound of fluid} = \frac{c}{g}(w_1' - w_2'). \tag{4}$$

When, as is usually the case, the direction of w_2' is opposite to that of w_1', the sign of w_2' must be considered negative and the algebraic difference $w_1' - w_2'$ in (2), (3), and (4) becomes the arithmetic sum $w_1' + w_2'$.

145. Single-stage Velocity Turbine.—In analyzing the action of the single-stage velocity turbine, it is convenient to start with an ideal frictionless turbine and then take up the case of the actual turbine.

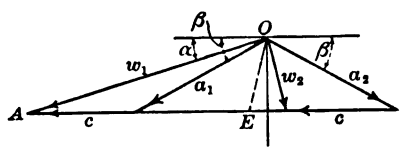


FIG. 71.

Let the jet emerge from the nozzle with the velocity w_1, Fig. 71, at an angle α with the plane of the wheel. Combining w_1 with c, the peripheral velocity of the blade, the velocity a_1 of the jet relative to the blade is obtained. The angle β between the direction of a_1 and the plane of the wheel determines the angle of the blade at entrance. If the blade is symmetrical, the exit relative velocity a_2 makes the same angle β with the plane of the wheel, and since the frictionless case is assumed, $a_2 = a_1$. Combining a_2 and c, the result is the absolute exit velocity w_2.

The energy of the jet with the velocity w_1 is $\frac{w_1^2}{2g}$ per pound

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of medium flowing; and the jet at exit has the energy $\frac{w_2^2}{2g}$. The work absorbed by the wheel per unit weight of steam in this ideal frictionless case is, therefore,

$$W = \frac{w_1^2 - w_2^2}{2g}, \tag{1}$$

and the ideal efficiency is

$$\eta = \frac{w_1^2 - w_2^2}{w_1^2}. \tag{2}$$

From the triangle OAE, Fig. 71, we have

$$w_2^2 = w_2^2 + (2c)^2 - 2w_1(2c)\cos\alpha; \tag{3}$$

whence $$w_1^2 - w_2^2 = 4(w_1 c\cos\alpha) - c^2). \tag{4}$$

Combining (2) and (4), we get,

$$\eta = 4\frac{c}{w_1}\left(\cos\alpha - \frac{c}{w_1}\right). \tag{5}$$

Equation (5) shows that the efficiency is greater the smaller the angle α; and that with a given constant angle α, the efficiency depends upon the ratio $\frac{c}{w_1}$. It is readily found that η takes its maximum value $\eta_{max} = \cos^2\alpha$ when

$$c = \tfrac{1}{2}w_1\cos\alpha. \tag{6}$$

As an example, let $\alpha = 20°$, whence $\cos\alpha = 0.9397$ and $\cos^2\alpha = 0.883$. If $w = 3600$ ft. per second, then to get the maximum efficiency 0.883, the ratio $\frac{c}{w_1}$ must be $\frac{1}{2}\cos\alpha = 0.47$, whence $c = 0.47 \times 3600 = 1692$ ft. per second, a value too high for safety. If c be given the permissible value 1200 ft. per second, we have $\frac{c}{w_1} = \frac{1}{3}$, and $\eta = 4 \times \frac{1}{3}(0.9397 - 0.3333) = 0.809$.

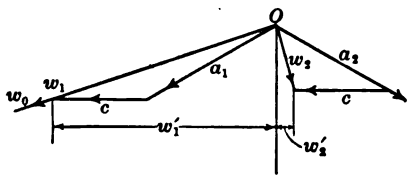


FIG. 72.

In the actual turbine, friction in the nozzle and blades reduces the efficiency considerably below the value given by (5). The velocity diagram with friction is shown in Fig. 72. The ideal jet velocity w_0 is reduced by friction in the nozzle to w_1. This actual jet velocity w_1 combined with velocity c gives the relative velocity a_1, as before. The exit relative velocity a_2 is smaller

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than a_1 because of friction in the blades, and as a result the absolute exit velocity w_2 is smaller than in the ideal case.

The work per pound of steam may be found from the velocity diagram either by calculation or by direct measurement. Having the components w_1' and w_2', the work per pound of steam is given by the expression

$$W = \frac{c}{g}(w_1' - w_2'). \tag{6}$$

This work may be compared with the work obtained from the ideal frictionless turbine given by (1) or with the energy of the jet per pound of steam, namely, $\frac{w_0^2}{2g}$.

146. Compounding.—For the pressure differences usually employed the jet velocity is necessarily high in a single stage turbine. Thus with a decrease of only 100 B. t. u. in the thermal head the velocity, after reduction by friction, is above 2000 ft. per second, and velocities above 3000 ft. per sec. might easily be obtained. The peripheral velocity for maximum efficiency is one-half of the component of the jet velocity in the direction of motion; hence in a single stage turbine this velocity ranges from 1000 to 1700 ft. per sec. The upper limit cannot be reached because with the best material available the stresses in the wheel become excessive when the peripheral speed exceeds about 1400 ft. per sec. Furthermore, these high peripheral speeds require higher rotative speeds than can be directly used by the machinery driven and some form of speed reduction is required.

It is generally desirable to keep the peripheral speed within the limits 200 to 700 ft. per sec. To accomplish this object without a sacrifice of efficiency some method of compounding is used.

1. *Pressure Compounding.*—The total drop of pressure $p_1 - p_2$ may be divided among several wheels, thus reducing the jet velocity at each wheel. If, for example, the change of thermal head is $i_1 - i_2$ and the expansion takes place in a single nozzle, the ideal velocity of the jet is $w = \sqrt{2gJ(i_1 - i_2)}$. If, however, $i_1 - i_2$ is divided equally among n wheels, the jet velocity is reduced to $w = \sqrt{\frac{2gJ}{n}(i_1 - i_2)}$; that is, the original jet velocity for the single expansion is divided by $\sqrt{n}$. All the vectors of

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the velocity diagram, including that which represents the peripheral velocity c, will be reduced to the same scale.

In the example of Art. 145, the peripheral velocity for maximum efficiency was found to be 1692 ft. per sec. With five stages the peripheral velocity would be $1692 \div \sqrt{5} = 757$ ft. per sec.; for twelve stages it would be $1692 \div \sqrt{12} = 488$ ft. per sec.

The general arrangement of a turbine with several pressure stages is shown in Fig. 73. Steam passes successively through orifices m_1, m_2, etc. in partitions b_1, b_2, etc., which divide the interior of the turbine into wheel chambers. The

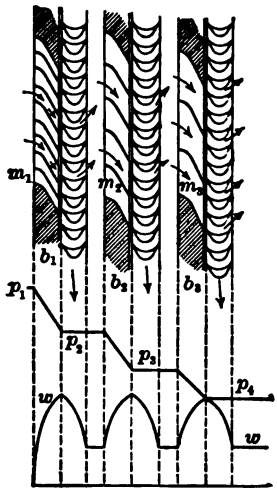


FIG. 73.

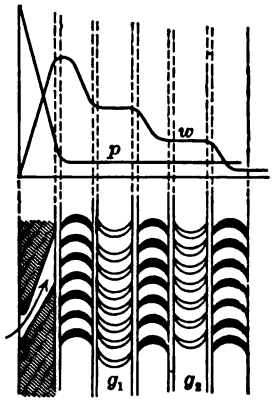


FIG. 74.

pressure drops from p_1 to p_2 in the first cell and the jet acts on the first wheel; then in passing through the orifice m_2 the pressure drops from p_2 to p_3; as a result the velocity is again increased and the jet passes through the second wheel. The pressure and velocity changes are shown roughly in the diagram at the bottom of the figure.

The method of compounding here described is called *pressure compounding*. Each drop in pressure constitutes a *pressure stage*.

2. *Velocity Compounding.*—The steam may be expanded in a single stage to the back pressure p_2, thus giving a relatively high velocity; and the jet may then be made to pass through a succession of moving wheels alternating with fixed guides. This system is shown diagrammatically in Fig. 74. The jet passes into the first moving wheel, where it loses part of its absolute

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velocity, as indicated by the velocity curve w. It then passes through the fixed guide g_1 with practically constant velocity and has its direction changed so as to be effective on entering the second moving wheel. Here the velocity is again reduced and the decrease of kinetic energy appears as work done on the wheel. This process may be again repeated, if desired, by adding a second guide and a third wheel. However, the work obtainable from a wheel is small after the second moving wheel is passed, and a third wheel is not usually employed.

The effect of velocity compounding in reducing the peripheral speed may be seen from a comparison of the ideal velocity

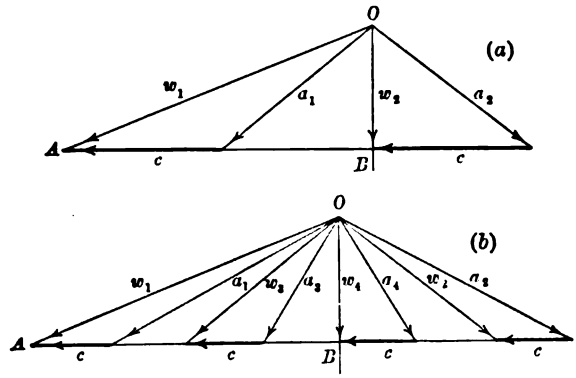


FIG. 75.

diagrams, Fig. 75, for a single stage turbine and for a turbine with two sets of moving blades. In the diagram (a) the peripheral velocity c is taken as one-half of the component of w_1 in the direction of c, a_1 and a_2 are symmetrical with respect to the axis, and as a result the exit velocity w_2 lies along the axis OB, and has its minimum value. In diagram (b) the four vectors w_1, a_1, a_2, w_2 constitute the velocity diagram for the first-moving blades. The exit velocity w_2 is turned in the direction w_3 by the fixed blades, and w_3 is the entrance velocity for the second set of moving blades. The remainder of the diagram is constructed as for a single stage turbine, and the exit velocity w_4 lies along the axis OB.

The segment AB, which represents w_1', the component of w_1, is double the velocity c in diagram (a) and four times the

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velocity c in diagram (b); that is, if two sets of moving blades are used the peripheral velocity for the single stage is divided by two. In general, if there are n sets of moving blades the required peripheral velocity is the peripheral velocity of the single stage divided by n.

3. *Combination of Pressure and Velocity Compounding.*—Evidently the two methods of compounding may be combined. In the Curtis turbine, for example, several pressure stages are

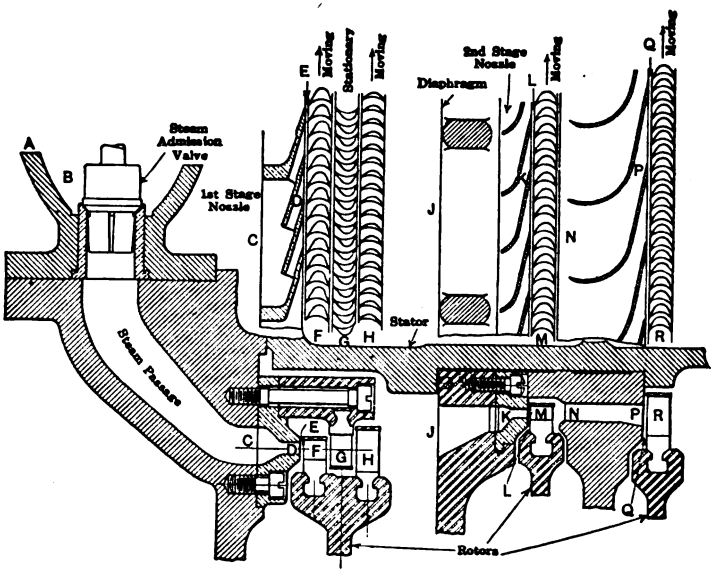


FIG. 76.

employed; in the earlier stages two sets of moving blades are used, that is, there is velocity compounding in each pressure stage. In the low-pressure stages the wheels may have only one set of moving blades. Fig. 76 shows the arrangement of nozzles and blades for one type of Curtis turbine.

147. Multiple-stage Velocity Turbine.—In the Rateau turbine, and in other turbines of similar construction, the principle of pressure compounding is employed. The turbine consists essentially of several de Laval turbines in series, running in separate chambers. See Fig. 73. The action of this type of turbine is conveniently studied in connection with a Mollier diagram, Fig 77. Let the initial state of the steam entering the turbine at the

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pressure p_1 be that indicated by the point A. If p_2 is the pressure in the first chamber, a frictionless adiabatic expansion from p_1 to p_2 is represented by AB, and the decrease in the thermal head $i_1 - i_2$ is represented by the length of the segment AB. Under ideal conditions, this drop in thermal head would all be transformed into kinetic energy of the jet of steam flowing into the chamber, and this in turn would be given up to the wheel.

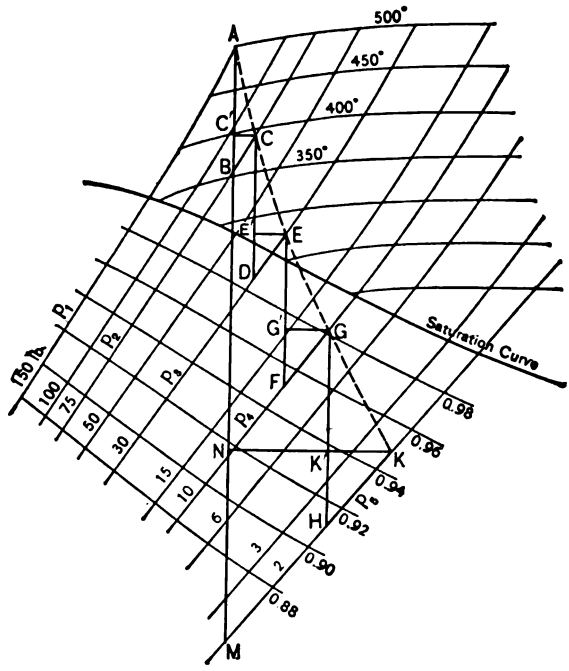


FIG. 77.

Actually, however, friction losses are encountered and the jet has an exit velocity w_2, thereby carrying away the kinetic energy $\frac{w_2^2}{2g}$. The velocity diagram for the single wheel under consideration is similar to that shown in Fig. 72. The work required to overcome friction in the nozzles and blades and the exit energy $\frac{w_2^2}{2g_1}$ are transformed into heat, and this heat, except a small fraction that is radiated, is expended in further superheating (or raising the quality of) the steam. Hence, instead of the final state B, we have a final state C on the same constant-pres-

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sure curve. The segment AC' represents the part of the drop of thermal head that is utilized by the wheel, while $C'B$ represents the part that is rendered unavailable by internal losses of various kinds.

The steam in the state C flows into the second chamber where the pressure is p_2. Frictionless adiabatic expansion would give the second state D, but the actual state is represented by the point E. Again CE' represents the effective drop of thermal head in this stage, while $E'D$ represents the part of the drop going back into the steam.

The same process is repeated in succeeding stages until finally the steam drops to condenser pressure in the last stage. The final state is represented by the point K, and the curve AEK represents the change of state of the steam during its passage through the turbine. The final state under ideal frictionless conditions is represented by point M. The segment AM represents the ideal drop of thermal head which, as has been shown, is equal to the available heat of the Rankine cycle. The segment AN represents the difference between the heat received by the turbine and the heat rejected to the condenser. If there were no losses other than the internal losses that are accounted for by the segment MN the heat represented by AN would be the heat transformed into work.

148. Turbine with both Pressure and Velocity Stages.—In certain turbines, notably the Curtis turbine, velocity compound-

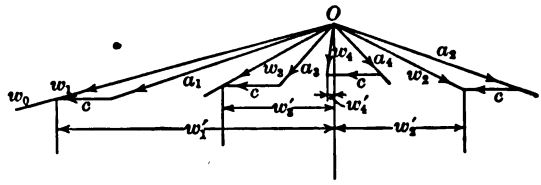


FIG. 78.

ing is employed. There are relatively few pressure stages, but in each chamber there are two or three rows of moving blades attached to the wheel rim and these are separated by alternate rows of guide blades, as shown in Fig. 74.

The velocity diagram for a single pressure stage with two velocity stages is shown in Fig. 78. The velocities in relation to the successive sets of blades are shown in Fig. 79. The jet emerges from the nozzle with an absolute velocity w_1, which is

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smaller than the ideal velocity w_0 because of friction in the nozzle. Combining w_1 with the peripheral velocity c of the first moving blade m_1, the result is the velocity a_1 of the jet relative to blade m_1. The angle α between a_1 and the plane of rotation is the proper entrance angle of the blade m_1. The exit relative velocity a_2, which is smaller than a_1, due to friction in the blade, is combined with the velocity c, giving the absolute exit velocity w_2 which makes the angle β with the plane of rotation. The jet enters the stationary guide blade s with the velocity w_2 and emerges with a smaller absolute velocity w_3. It then enters the second moving blade m_2. Combination of w_3 with c gives the relative velocity a_3 and the entrance angle γ for the blade m_2. The exit velocity a_4 is determined from a_3 and the friction in the blade, and by combining a_4 and c, the absolute exit velocity w_4 is obtained.

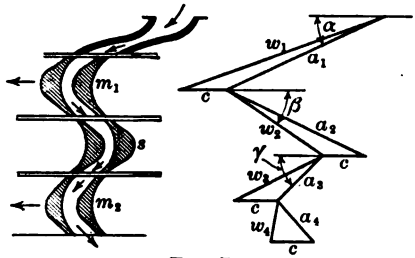


FIG. 79.

In the diagram, Fig. 79, the blades have been taken as symmetrical. Sometimes, however, the exit angles of the last sets of blades are made smaller than the entrance angles. The diagram can easily be modified to suit this condition.

The work per pound of steam for this wheel is readily determined from the velocity diagram. From the first set of blades m_1 the work $\frac{c}{g}(w_1' - w_2')$ and from the second set of blades m_2 the work $\frac{c}{g}(w_3' - w_4')$ is obtained. Hence the total work per pound of steam is

$$W = \frac{c}{g}(w_1' - w_2' + w_3' - w_4'). \qquad (1)$$

Care must be taken that w_2' and w_4' be given their proper algebraic signs.

The change of state of the fluid as it passes through the turbine may be shown by the Mollier diagram as indicated in Fig. 77. Starting with an initial state indicated by point A, the available drop from the initial pressure p_1 to the pressure p_2 in the first

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chamber is represented by AB. The heat utilized in useful work W as given by (1) is represented by AC'. Hence projecting C' horizontally to C on the line of constant pressure p_2, we get the state of the steam as it enters the second stage nozzles.

149. The Pressure Turbine.—The characteristic features of the pressure or reaction turbine are illustrated in Fig. 80. The guide vanes attached to the outside casing alternate with the

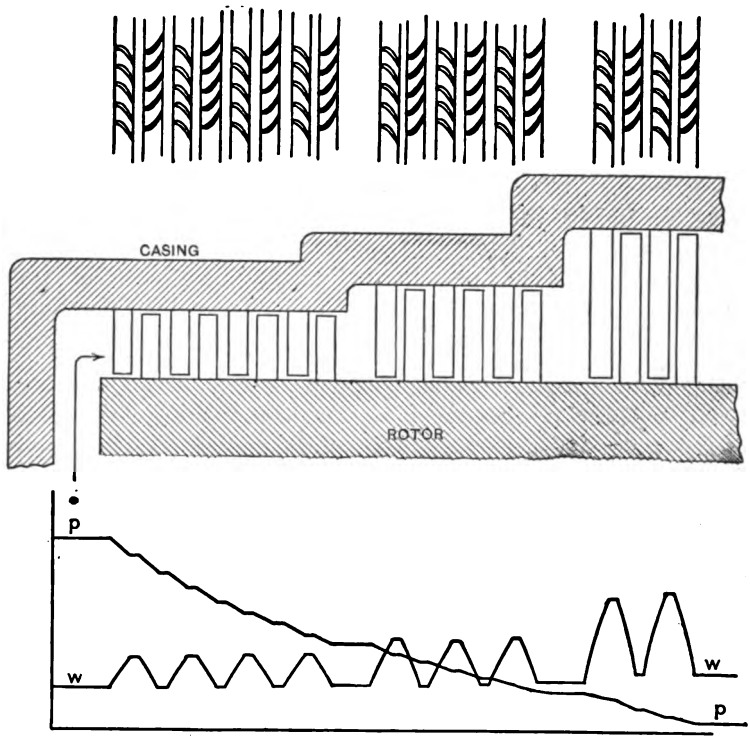


FIG. 80.

moving blades attached to the rotating element. As shown by the rows of developed blades, the blades are unsymmetrical; the angle between the blade tip and the axis of the turbine is small at entrance and much larger at exit. Partial peripheral admission of the steam, as in the velocity turbine, is impossible, and the guide blades must extend around the entire circumference of the casing. The turbine "runs full," and the pressure drops

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continuously through both stationary and moving blades. The curve *pp* shows the variation of pressure through the turbine. Due to the drop of pressure, the absolute velocity of the steam increases in the guide vanes, as shown by the curve of velocity *ww*; likewise the velocity relative to the blade increases in the moving blades, but the absolute velocity decreases.

The specific volume of the steam increases as the pressure drops and becomes very large near the condenser end of the turbine. At any section of the turbine the volume of steam flowing is the product of the area of the passages and the steam velocity; hence the increasing volume may be accommodated either by increasing the area, the steam velocity, or both. The annular space between rotor and casing is increased by increasing the pitch diameter and the length of the blades in successive stages. However, for constructive reasons, the increase is not uniform; several stages are grouped together, these having about the same pitch diameter and blade length. The annular space between rotor and casing forms, in effect, a large diverging nozzle. The steam velocity is also increased in the low pressure stages, as shown by the curve *ww*.

150. Velocity Diagram.—The fact that the pressure falls continuously, both through the guide blades and the moving blades, makes the velocity diagram essentially different from that of the velocity turbine. Referring to Fig. 81, let w_1 denote the absolute velocity of the steam entering the stationary blade s_1, and w_2 the absolute exit velocity. If there were no change of pressure, w_2 would be smaller than w_1 because of friction; but the drop in pressure Δp causes a decrease in thermal potential Δi, and as a result, there is an increase of velocity given by the relation

$$\frac{w_2^2 - w_1^2}{2g} = J(1 - y)\Delta i. \qquad (1)$$

Thus the exit velocity w_2 is greater than the entrance velocity w_1. Combining w_2 with c, the velocity of the moving blade, we obtain a_1, the velocity of entrance relative to the moving blade. The pressure drops through the moving blades also; hence as a result the velocity of exit a_2 is greater than a_1, just as w_2 is greater than w_1. Combining a_2 with c, the result is w_1, the absolute velocity of entrance into the next row of fixed blades.

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The work done in any single stage, consisting of one set of stationary blades and one set of moving blades, is obtained from the velocity diagram for that stage in the usual way. Thus, if we have the diagram shown in Fig. 82 for a particular stage, the work per pound of steam for that stage is given by the product

$$\frac{c}{g}(w'_2 - w'_1).$$

If the fixed and moving blades have the same entrance angles and exit angles, it may be assumed that the velocity diagram has the symmetrical form shown in Fig. 82; that is, $w_1 = a_1$ and $w_2 = a_2$. In this case the preceding expression for work per pound becomes

$$W = \frac{c}{g}(2w_2 \cos\theta - c), \qquad (2)$$

in which θ is the angle between the vectors w_2 and c.

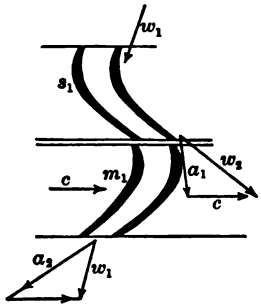


FIG. 81.

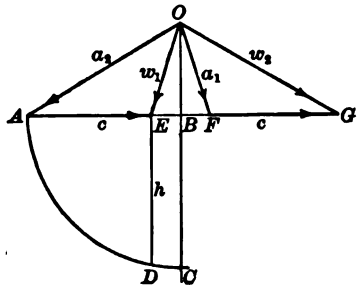


FIG. 82.

The following graphical construction is useful. Using point B as a center and with a radius BA let a circular arc ADC be described, and from E let a perpendicular be dropped cutting this arc in D. Denoting the length ED by h, we have

$$h^2 = AE \times EG = c\,(w_2' - w_1').$$

It follows that the work per pound of steam is given by the expression $\frac{h^2}{g}$ provided h is measured to the same scale as the velocity vectors w_1, w_2.

The ratio of the peripheral velocity c to the steam velocity w_2 entering the moving blades may be varied within rather wide limits. The value 0.6 is usual, but in the last stages, where w_2

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is necessarily high, the ratio may be as low as 0.3 or 0.4. The angle θ may vary from 20° to 30°.

EXAMPLE. In the first stage of a pressure turbine the velocities are $c = 150$ ft. per sec. and $w_2 = 250$ ft. per sec.; and $\theta = 22\frac{1}{2}°$. The work obtained from this stage is

$$\frac{150}{32.2}(2 \times 250 \times 0.9239 - 150) = 1453 \text{ ft. lb.}$$

The heat required for this work is 1.87 B. t. u., and this is the net decrease in thermal potential after deducting various losses.

In the last stage let $c = 360$ and $w_2 = 900$ ft. per sec. Then the work is

$$\frac{360}{32.2}(2 \times 900 \times 0.9239 - 360) = 14567 \text{ ft. lb.},$$

corresponding to a net drop in thermal potential of 18.72 B. t. u.

It appears that with the low velocities employed in the pressure turbine the work per stage is small, especially in the earlier stages, and that in consequence a large number of stages is required.

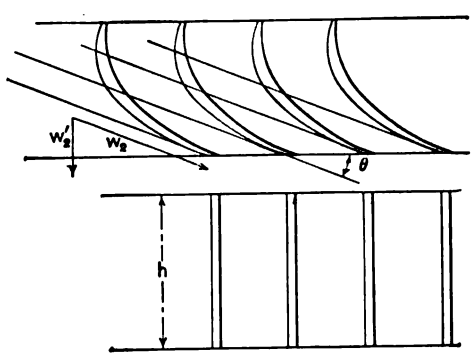


FIG. 83.

151. Blade Lengths.—The fact that the pressure turbine runs full imposes a restriction on the choice of blade dimensions. The length of the blade in a given stage cannot be selected at will, but must be made such that the annular space for the passage of the steam shall have the proper area to pass the required volume of steam at the pressure and velocity existing in that stage.

Referring to Fig. 83, let h denote the length of the blade and d the pitch diameter of the barrel, both in inches. Then the area of the annulus between rotor and casing is

$$\frac{\pi dh}{144} \text{ sq. ft.}$$

All of this area is not effective, however, as the blades must occupy some of it; the effective area may be taken as

$$\frac{k\pi dh}{144},$$

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where k is a coefficient whose value lies between 0.70 and 0.85. The steam velocity along the blade is w_2 and the component of this at right angles to the annular space is $w_2' = w_2 \sin \theta$; hence the volume of steam flowing through the stage per second is

$$\frac{k\pi dh}{144} w_2 \sin \theta.$$

But if M is the weight of steam flowing per second and v is the specific volume, the product Mv is the volume flowing; hence

$$\frac{k\pi dh}{144} w_2 \sin \theta = Mv,$$

or

$$h = \frac{144\ Mv}{k\pi d w_2 \sin \theta}. \qquad (1)$$

EXAMPLE. A pressure turbine driving a 2000-kw. generator uses 9 lb. of steam per second. At a certain stage the pressure is 37 lb. per sq. in., the quality is 0.97 and the steam velocity is assumed to be 550 ft. per sec. The pitch diameter of the wheel is 20 in., the exit angle is 22½°, and k may be taken as 0.8. Required the length of blade.

From the steam table v = 10.97 cu. ft. per lb. Therefore

$$h = \frac{144 \times 9 \times 10.97}{0.8 \times 3.1416 \times 20 \times 550 \times 0.3827} = 1.34 \text{ in.}$$

152. Combination Turbines.—In the high-pressure stages of a pressure turbine the blades are necessarily short, the length being as small as ½ inch. Radial clearance between the tips of the blades and the casing (or rotor) must be provided; and since the pressure drops continuously, part of the steam passes over the tips of the blades without doing work. Evidently the leakage is relatively greater in the stages with the shorter blades, that is, at the high-pressure end of the turbine.

To obviate the leakage loss, combined velocity and pressure turbines have been constructed. The Westinghouse double-flow turbine, Fig. 84, is of the combined type. The steam is first admitted through nozzles to an impulse wheel, which has usually two sets of moving blades. The steam passing from this wheel is then divided, one half flowing to the reaction blades on the right-hand drum, the other half to a similar set of blades on the left hand drum. The greater part of the pressure drop occurs

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in the impulse wheel, so that the specific volume of the steam entering the reaction elements is large enough to require a reasonable blade length. Furthermore, the division of the steam between the reaction elements reduces the blade lengths required in the last stages, where the steam volume is excessive.

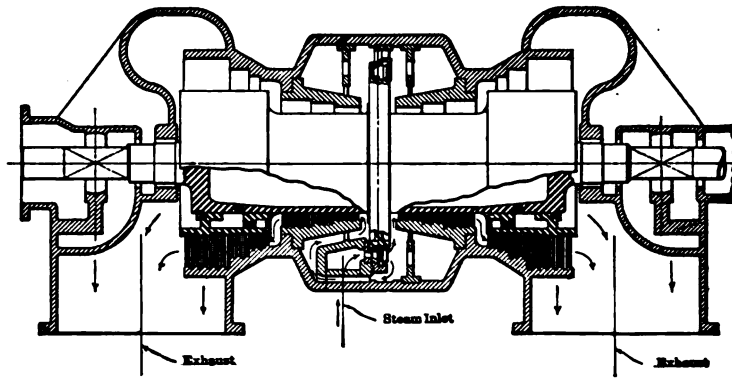


FIG. 84.

153. High Vacuum and Superheat.—Obviously the steam turbine can utilize a high vacuum to better advantage than the reciprocating engine. In the case of the engine, the economical limit of vacuum is about 26 in. of mercury; with steam turbines, the vacuum is from 27 to 29 in. based on a 30-in. barometer, that is, the condenser pressure is 1 to 3 in. of mercury. Tests indicate that the saving in steam consumption is from 5 to 8 per cent. for each inch increase of vacuum, and somewhat more than this for low pressure turbines.

High superheat may be used advantageously in the steam turbine since there are no rubbing parts in contact with the steam. It is desirable, however, to keep the high-temperature steam from contact with the casing and turbine blades; hence with high superheat the entering steam should have its temperature and pressure reduced by expansion in the first-stage nozzles. The use of superheated steam is advantageous in reducing the erosion of the turbine blades by the water in the steam and in reducing the windage losses of the rotor. As regards economy, superheating is less effective than increase of vacuum in the reduction of the steam consumption.

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154. Low-Pressure Turbines.—The advantage of the steam turbine in its ability to take care of large volumes of steam at low pressure has been mentioned. A consideration of the division of the available heat between the high-pressure and the low-pressure range shows clearly the great advantage of the turbine in this respect. Suppose, for example, that steam is furnished at a pressure of 180 lb. and temperature of 560° F. and that the condenser pressure is 2 in. of mercury; then the available heat is 371 B. t. u. of which 210 B. t. u. is the decrease of thermal potential between the initial state and atmospheric pressure, and the remaining 161 B. t. u., about 43 per cent. of the total, is the decrease from atmospheric pressure to the condenser pressure. The reciprocating engine cannot utilize more than a small part of the 161 B. t. u., whereas the turbine is capable of utilizing a large per cent. of it. An excellent combination consists of a reciprocating engine exhausting at or somewhat above atmospheric pressure with a low-pressure turbine taking its steam from the engine. In some instances large power plants having reciprocating condensing engines have been remodeled by the interposition of turbines between the engines and condensers. The capacity of the plant has been doubled by such a change.

Low-pressure turbines may be employed advantageously to utilize an intermittent supply of exhaust steam such as is furnished by the non-condensing engines of rolling mills, forging plants, etc. To keep a constant supply of steam a *regenerator* or *accumulator* is placed between the engines and the turbine. The exhaust steam is led into a vessel containing a large mass of water; when the steam supply exceeds the requirements of the turbine some of the entering steam is condensed, and when the supply is deficient some of the water is vaporized.

155. Losses in the Steam Turbine.—The principal losses of available heat in the steam turbine are those that arise from the irreversible conversion of work into heat. Of such losses the following may be mentioned.

(*a*) Loss due to friction between the steam and the nozzles, guides, and moving buckets.

(*b*) Loss due to windage; that is, the friction between a rotating wheel and the steam in the cell.

(*c*) Loss due to leakage from a stage into a succeeding stage in

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which the pressure is lower. This process is, in effect, an instance of throttling.

(*d*) Loss due to exit velocity. If w_2 is the absolute exit velocity from a moving wheel the kinetic energy $\frac{{w_2}^2}{2g}$ is wholly or partly transformed into heat.

These losses differ from those encountered in the steam engine in one essential feature. The heat generated passes into the

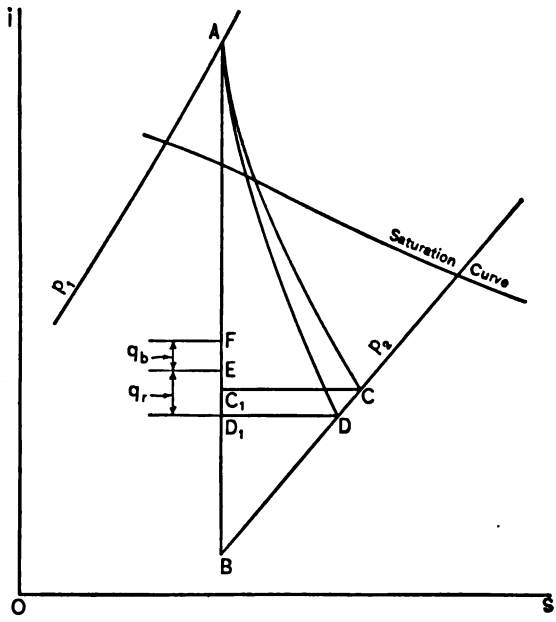


FIG. 85.

flowing steam and increases its quality (or temperature, if superheated).

In addition, there are direct losses of heat. Some heat is radiated from the turbine, and heat is carried out by the water drained from the turbine. The heat equivalent of the work done against the friction of the bearings is carried away by the oil and water used in the bearings.

The course of the curve showing the change of state of the steam in its passage through the turbine will depend on the

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amount of the various losses. Taking the *is*-plane, Fig. 85, let A denote the initial condition of the steam entering the turbine at pressure p_1; then AB represents frictionless adiabatic expansion to pressure p_2, and the length of the segment AB represents the available heat. The losses of the first kind are accompanied by the generation of heat H, the entropy is accordingly increased by $\int \frac{dH}{T}$, and the expansion curve, assuming that there are no losses of heat by radiation, takes the course AC. Thus AC is an adiabatic and the increase of entropy C_1C is due to the irreversible conversion of work into heat H. In this case the difference $i_a - i_c$ ($= AC_1$) is the difference between the heat absorbed from the boiler and the heat rejected to the condenser, and it is therefore the heat transformed into work.

Consider now the losses of heat by radiation. If heat leaves the steam during its course through the turbine, the effect of this process by itself is to decrease the entropy. The net result of the two processes, generation of heat H through friction and rejection of heat Q to the surroundings, is an expansion curve like AD lying to the left of AC. The segment AD_1 now represents the difference between the heat absorbed from the boiler and the heat rejected to the condenser; but in this case, this difference includes the heat q_r leaving the steam as well as the heat (q) transformed into work. That is,

$$i_a - i_d = (q) + q_r$$

If segment D_1E represents q_r, then segment AE represents the heat (q) transformed into work; hence laying off segment EF to represent q_b, the heat equivalent of the work expended at the bearings, the segment AF represents finally the heat equivalent of the net work that is delivered at the shaft.

The ratio $AE : AB$ gives the efficiency η_2 of the turbine based on indicated horsepower, and the ratio $AF : AB$ the efficiency based on brake horsepower.

A test of a steam turbine gives the following data: The horsepower delivered at the brake, the weight of steam used per unit of time, the initial condition of the steam entering the turbine, and the final state of the steam in the condenser. From these data the points A, B, D, D_1, and E may be located on

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the Mollier chart, and an estimate of the losses may be made. Information thus obtained from tests may be used to predict the results that may be expected in a new design.

EXAMPLE. A turbine receives steam at a pressure of 180 lb. per sq. in. superheated to 560° F., the condenser pressure is 2 in. of mercury and the quality of the exhaust steam as determined by a test is 0.92. The steam consumption as shown by the test is 10.9 lb. per brake horsepower hour.

From the Mollier chart the thermal potential for the initial state is $i_a = 1302.2$ B. t. u., and with frictionless adiabatic expansion to $p_2 = 2$ in. of mercury, the final potential is $i_b = 931.2$ B. t. u. Hence the available heat is $1302.2 - 931.2 = 371$ B. t. u. For the state of the steam at exhaust, pressure of 2 in., quality 0.92, the thermal potential is $i_d = 1022$ B. t. u., and the segment AD_1 represents the decrease $1302.2 - 1022 = 280.2$ B. t. u. The heat equivalent of the work delivered at the shaft per pound of steam is $2546 \div 10.9 = 233.6$ B. t. u. This is represented by segment AF, and therefore segment D_1F represents the heat $280.2 - 233.6 = 46.6$ B. t. u., which is the sum of q_r and q_b. The efficiency of the turbine based on net horsepower at the shaft is $233.6 \div 371 = 0.63$.

EXERCISES

1. In a single-stage velocity turbine the velocity of the jet is 2980 ft. per sec. and the angle between the direction of the jet and the plane of rotation is 22½°. (*a*) Find the peripheral velocity for maximum efficiency. (*b*) Find the efficiency with a peripheral speed of 1120 ft. per sec.

Ans. (*a*) 1377 ft. per sec. (*b*) 0.831

2. With the following data draw the velocity diagram for a single-stage velocity turbine and find the work per pound of steam. Speed of jet, 3200 ft. per sec.; peripheral speed 1050 ft. per sec.; relative velocity at exit 10 per cent. less than at entrance; angle between jet and plane of rotation 22°.

Ans. 118,900 ft.-lb.

3. Devise a system of compounding that will give a peripheral velocity of about 450 ft. per sec. when the peripheral velocity of the single-stage turbine for maximum efficiency is 1720 ft. per sec.

4. In one of the stages of a compound turbine the wheel carries two sets of blades and the casing an intermediate set of guide blades. The velocity of the steam jet is 2100 ft. per sec. and the angle between the direction of the jet and the plane of rotation is 22½°. The peripheral velocity of the moving blades is 420 ft. per sec. In each set of blades the loss of velocity through friction is 10 per cent. Taking the entrance and exit angles equal, draw the velocity diagram (see Fig. 78). Determine the proper entrance angles for each of the three sets of blades. Find the work per pound of steam, and compare with the kinetic energy of the jet.

Ans. 48,470 ft.-lb.; 70.7 per cent. of energy of jet.
$\alpha = 27° 52'$; $\beta = 37° 21'$; $\gamma = 56° 21.5'$.

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5. A turbine is supplied with saturated steam at a pressure of 150 lb. per sq. in., and the condenser pressure is 3 in. of mercury. Three pressure stages are to be used and the intermediate pressures are to be such that in each of the first two stages 30 per cent. of the work is delivered and in the last stage 40 per cent. Determine approximately the pressures in the three stages.

6. In the intermediate stages of the three drums of a pressure turbine the velocities w_2 and c (see Fig. 82) have the following values.

	1st	2nd	3d
w_2	430	600	850 ft. per sec.
c	210	300	425 ft. per sec.

The exit angle α for each stage may be taken as $22\frac{1}{2}°$. Find for each stage the heat equivalent of the external work.

Ans. 4.90 B. t. u.: 9.69 B. t. u.; 19.44 B. t. u.

7. The condition of the steam flowing through the three stages is as follows:

	1st	2nd	3d
Pressure	105	28	5 lb. per sq. in.
Quality	0.98	0.94	0.91

The turbine takes 3000 rev. per min. and the weight of steam flowing is 8.2 lb. per sec. With $k = 0.77$, find the blade lengths required.

Ans. 0.77 in.; 1.28 in.; 6.83 in.

8. A reciprocating engine is supplied with saturated steam at 170 lb. per sq. in. and exhausts at a pressure of 16 lb. per sq. in. If a turbine is added and the condenser pressure is 2.2 in. of mercury, what is the increase in the available heat? Ans. 85.5 per cent.

9. In a test of a steam turbine the following data were obtained: Steam supplied at a pressure of 205 lb. per sq. in. and temperature of 560° F. Back pressure 1.1 in. of mercury. Consumption of steam 12.1 lb. per kilowatt-hour. Find the efficiencies η_1 and η_2, and the heat consumed per kw.-min. Ans. $\eta_1 = 0.226$; $\eta_2 = 0.692$; 252 B. t. u.

10. If, in the test, the quality of steam in the exhaust was 0.89, what was the sum $q_r + q_b$, the heat radiated to the surroundings per pound of steam? Ans. 37 B. t. u.

REFERENCES

For the theory of the steam turbine, the design and construction, reference may be made to the works of Stodola, Thomas, Jude, Moyer, Peabody, and Row.

Numerous papers on the applications of steam turbines and the use of low-pressure turbines may be found in the Transactions of the American Society of Mechanical Engineers, also in Power.

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CHAPTER XIII

COMPRESSED AIR

156. Air Compressors.—Compressed air finds many applications in the engineering field. Air at low pressure is used for the ventilation of buildings, for supplying furnaces, forges, and cupolas. In shops compressed air is used for hoists, drills, and for the operation of small tools; in mining and tunnelling it is used to operate rock drills and for other purposes. Finally, compressed air may be used for the transmission of power over considerable distances.

The type of compressor employed depends upon the pressure required. For pressures up to 10 or 12 oz. per sq. in. centrifugal blowers are used; for somewhat higher pressures positive rotary blowers are usually employed. Centrifugal compressors, or turbo-blowers, as they are called, may be used for still higher pressures, say up to 35 lb. per sq. in. To produce the higher pressures required in most compressed-air installations and for the transmission of power reciprocating piston compressors are employed.

The piston air compressor consists simply of a cylinder with a reciprocating piston and inlet- and exit-valves at each end. The valves are sometimes mechanically operated but usually they are actuated by the air itself. On the suction stroke air is drawn into the cylinder through the inlet-valves, on the return stroke these valves close and the air is compressed until the pressure slightly exceeds the external pressure in the air receiver, when the exit-valves open, and during the remainder of the stroke the air is pushed from the cylinder into the receiver.

Engines for using compressed air differ in no essential particular from steam engines.

157. Cycle of Air-Compressor and Engine.—For a clear understanding of the problems involved in power transmission by compressed air it is necessary to trace out the various changes of state of the air in its passage through the compressor, the

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pipe line, and the engine. For this purpose we use the pV- and TS-diagrams, Fig. 86 and 87. It is assumed that the air enters the compressor at atmospheric pressure and temperature, this state being represented by the point A. Adiabatic compression of the air is represented by AB. The point B represents the condition in the receiver, pressure p_2 and absolute temperature T_2. The changes of state in the pipe line are represented by BC and CD; first there is loss of heat at nearly constant pressure and then loss of pressure at nearly constant temperature. See Art. 119. The air enters the air motor in the state represented by point D (pressure p_2) and expands adiabatically to pressure p_1, as indicated by DE. Finally, the air at atmospheric

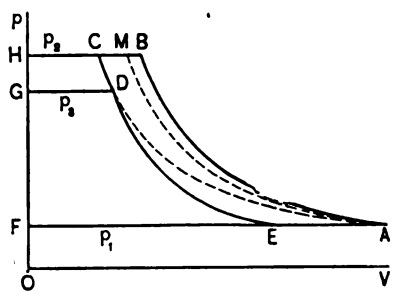


FIG. 86.

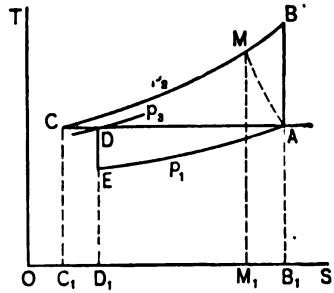


FIG. 87.

pressure and at the low temperature indicated by point E absorbs heat from the atmosphere at constant pressure and thus returns to the initial state A.

The figure $ABHF$ is the indicator diagram of the compressor, assuming there is no clearance; and likewise $GDEF$ is the indicator diagram of the air engine. The areas of these two diagrams represent, respectively, the work done by the compressor and the work received from the engine; therefore the area $ABHGDE$ represents the loss of work in the transmission.

158. Work of the Compressor.—An expression for the work represented by the indicator diagram $ABHF$ is obtained as follows. Let p_1, V_1 and p_2, V_2, respectively, denote the pressures and volumes at states A and B; then since AB is an adiabatic, its equation is

$$p^{\frac{1}{k}}V = p_1^{\frac{1}{k}}V_1 = p_2^{\frac{1}{k}}V_2 = C. \qquad (1)$$

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The required area is that between the curve AB and the p-axis, and this is obtained by the summation of elements of the form vdp; hence the work W_c of the compressor is

$$W_c = -\int_{p_1}^{p_2} V dp. \tag{2}$$

The negative sign must be used because in passing from A to B the work, being done *on* the air, is negative, and a negative dW is associated with a positive dp, and vice versa. Eliminating V by means of (1), equation (2) becomes

$$W_c = -C\int_{p_1}^{p_2} p^{-\frac{1}{k}} dp = \frac{Cp_1^{1-\frac{1}{k}} - Cp_2^{1-\frac{1}{k}}}{1-\frac{1}{k}}$$

$$= \frac{p_1^{\frac{1}{k}} V_1 p_1^{1-\frac{1}{k}} - p_2^{\frac{1}{k}} V_2 p_2^{1-\frac{1}{k}}}{1-\frac{1}{k}} = \frac{k}{k-1}(p_1V_1 - p_2V_2). \tag{3}$$

Equation (3) may be given another form which is more convenient for certain purposes. Thus

$$W_c = \frac{k}{k-1} p_1V_1\left(1 - \frac{p_2}{p_1}\frac{V_2}{V_1}\right) = \frac{k}{k-1} p_1V_1\left[1 - \frac{p_2}{p_1}\left(\frac{p_1}{p_2}\right)^{\frac{1}{k}}\right]$$

$$= \frac{k}{k-1} p_1V_1\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}\right]. \tag{4}$$

Let p_3, V_3 and p_4, V_4 denote, respectively, the pressures and volumes at points D and E; then by a similar process we find for the work of the air engine

$$W_e = \frac{k}{k-1}(p_3V_3 - p_4V_4) = \frac{k}{k-1} p_3V_3\left[1 - \left(\frac{p_4}{p_3}\right)^{\frac{k-1}{k}}\right].$$

Since points A and D lie on an isothermal,

$$T_A = T_D,$$

and $$p_1V_1 = p_3V_3; \qquad \text{also} \quad p_4 = p_1.$$

Hence the preceding equation becomes

$$W_e = \frac{k}{k-1} p_1V_1\left[1 - \left(\frac{p_1}{p_3}\right)^{\frac{k-1}{k}}\right]. \tag{5}$$

In equations (4) and (5) V_1 may be taken as the volume of air entering the cylinder per stroke or the volume entering per

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minute; in the former case W gives the work per stroke, in the latter case, the work per minute.

The work may also be expressed in terms of the weight of air entering the cylinder and the initial and final temperatures. If T_1 and T_2 denote the absolute temperatures at A and B, respectively, and M the weight of air, then

$$p_1V_1 = MBT_1, \quad p_2V_2 = MBT_2,$$

and (3) may be reduced to the form

$$W_c = \frac{k}{k-1}MB(T_1 - T_2). \tag{6}$$

But $$\frac{k}{k-1}B = Jc_p;$$

hence $$W_c = -JMc_p(T_2 - T_1). \tag{7}$$

The product $Mc_p(T_2 - T_1)$ gives, however, the heat rejected by the air in cooling from T_2 to T_1, and this heat is represented by the area B_1BCC_1 under the constant pressure curve BC, Fig. 87. The area B_1BCC_1 therefore represents the work of the air compressor, and in the same way it is shown that the area D_1EAB_1 represents the work of the air engine. The loss of work is represented by the area D_1EABCC_1, of which part is due to the needless rise of temperature during compression and part to the loss of pressure in the pipe. Various methods of reducing this loss will be discussed.

159. Water-jacketing.—Unless some provision is made for withdrawing heat during the compression, the temperature will rise according to the adiabatic law. Ordinarily the energy stored in the air due to its increase of temperature is never utilized because during the transmission of the air through the mains heat is lost to the surroundings and the temperature falls to the initial value. Hence a rise in the temperature during compression indicates a useless expenditure of work. The water jacket prevents in some degree this rise in temperature and decreases the work required for compression. The curve AB (Fig. 86) represents adiabatic compression. If the compression could be made isothermal, the curve would be AC, less steep than AB, and the work of the compressor would be reduced by the area ABC. The water jacket gives the curve AM lying between AB and AC, and the area ABM represents the saving

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in work. Because of the water jacket the value of the exponent n in the equation $pV^n = \text{const.}$ lies somewhere between 1 and 1.40. Under usual working conditions, n is about 1.3 to 1.35.

The work of the compressor when the compression curve follows the law $pV^n = \text{const.}$ is

$$W_c = \frac{n}{n-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}\right], \tag{1}$$

or

$$W_c = \frac{n}{n-1}(p_1 V_1 - p_2 V_2). \tag{2}$$

These expressions are obtained by substituting n for k in the discussion of the preceding article.

On the Ts-plane the change of state during compression with a water jacket is represented by the curve AM, Fig. 87, and the area B_1AMM_1 represents the heat absorbed by the water during the process. The specific heat corresponding to the exponent n is $c_n = c_v \frac{k-n}{1-n}$ (Art. 38). Hence

$$\text{area } B_1AMM_1 = Mc_v \frac{k-n}{1-n}(T_2 - T_1), \tag{3}$$

and

$$\text{area } M_1MCC_1 = -Mc_p(T_2 - T_1). \tag{4}$$

Adding these expressions the heat represented by the area under the path AMC is

$$\begin{aligned} Q &= M\left(c_p - c_v \frac{k-n}{1-n}\right)(T_1 - T_2) \\ &= M\frac{n}{n-1}(c_p - c_v)(T_1 - T_2) \\ &= \frac{n}{n-1} ABM(T_1 - T_2) \\ &= A\frac{n}{n-1}(p_1 V_1 - p_2 V_2). \end{aligned} \tag{5}$$

Comparing (5) and (2) it is seen that the area under the path AMC represents the work of the compressor. The area of the triangle ABM, Fig. 87, represents, therefore, the saving due to the water jacket.

160. Multi-Stage Compression.—If the final pressure exceeds 80 or 90 lb. per sq. in. the compression is carried out in two or more stages. In a two-stage compression, for example, the air is first compressed from the initial pressure p_1 to an intermediate pressure p', it is then passed through an intercooler where the

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temperature is reduced nearly or quite to the initial temperature, and it is then compressed from the pressure p' to the final pressure p_2 in a second cylinder. For very high values of p_2, three, or even four, stages may be used.

Multi-stage compression has several advantages. The total work of compression is reduced; the mechanical stresses in the compressor are smaller than in a single-stage compressor of the same capacity; and the temperature range in each cylinder is less than the range in a single cylinder.

Fig. 88 and 89 show the pV- and TS- diagrams for a two stage compression. The curve AP represents the compression in the first cylinder to the intermediate pressure p', curve PQ the

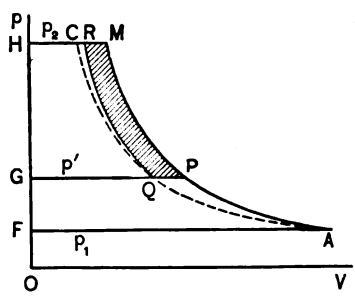


Fig. 88.

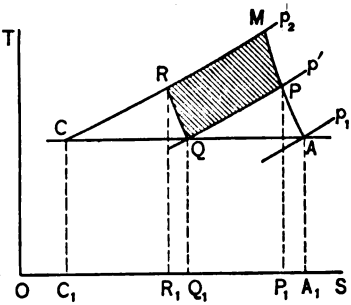


Fig. 89.

cooling of the air at constant pressure to the initial temperature T_1, curve QR the compression from p' to p_2 in the second cylinder. On the pV-plane $APGF$ is the indicator diagram for the first compressor, $QRHG$ the indicator diagram for the second. For a single-stage compressor the indicator diagram is $AMHF$; hence, the saving of work is represented by the area $PQRM$.

On the TS-plane the area A_1APP_1 represents the heat given up to the first water jacket, area P_1PQQ_1 the heat rejected to the water in the intercooler, area Q_1QRR_1 the heat given up in the second water jacket, and area R_1RCC_1 the heat given up to the surroundings as the air flows along the main. The total area under the path $APQRC$ represents the work of the compressor, and the area $PQRM$ represents the saving effected by compression in two stages.

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According to the preceding formulas, the work done in the first cylinder is given by the expression

$$W_1 = \frac{n}{n-1} p_1 V_1 \left[1 - \left(\frac{p'}{p_1}\right)^{\frac{n-1}{n}}\right];$$

and the work done in the second cylinder by the expression

$$W_2 = \frac{n}{n-1} p' V' \left[1 - \left(\frac{p_2}{p'}\right)^{\frac{n-1}{n}}\right],$$

where V' is the volume indicated by point Q (Fig. 89). But since point Q is on the isothermal AC, we have $p'V' = p_1V_1$, and, therefore,

$$W_2 = \frac{n}{n-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p'}\right)^{\frac{n-1}{n}}\right].$$

The total work is, consequently,

$$W_2 + W_1 = \frac{n}{n-1} p_1 V_1 \left[2 - \left(\frac{p_2}{p'}\right)^{\frac{n-1}{n}} - \left(\frac{p'}{p_1}\right)^{\frac{n-1}{n}}\right]. \qquad (1)$$

The work required is numerically a minimum when the expression

$$\left(\frac{p_2}{p'}\right)^{\frac{n-1}{n}} + \left(\frac{p'}{p_1}\right)^{\frac{n-1}{n}}$$

has a maximum value. Note that p_1 and p_2 are fixed, while p' is variable. Placing the derivative of this expression withrespect to p' equal to zero, it is found that the maximum value is given when

$$p' = \sqrt{p_1 p_2}, \qquad (2)$$

or when

$$\frac{p_2}{p'} = \frac{p'}{p_1} = \left(\frac{p_2}{p_1}\right)^{\frac{1}{2}}. \qquad (3)$$

If there are three stages with intermediate pressures p' and p'' the condition for minimum work of compression is

$$\frac{p_2}{p''} = \frac{p''}{p'} = \frac{p'}{p_1} = \left(\frac{p_2}{p_1}\right)^{\frac{1}{3}}. \qquad (4)$$

Combining (3) and (1), the total work of compression, provided the intermediate pressure p' is given by (2), is

$$W_c = \frac{2n}{n-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{2n}}\right]. \qquad (5)$$

Likewise for three stages

$$W_c = \frac{3n}{n-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{3n}}\right]. \qquad (6)$$

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161. Reheating.—A considerable increase of work may be obtained from the air motor by heating the air at constant pressure before it enters the motor. The simplest method of heating consists in passing the air through a coil of pipe within a furnace fired with coal, gas, or liquid fuel. The air may also be heated by passing it through steam or hot water in a boiler or by injecting steam into the main near the motor.

The changes of state when reheating is employed are shown on the TS-plane in Fig. 90. The processes AM, MC, and CD are the same as described in connection with Fig. 87. The air in the state indicated by point D enters the heater and is heated at the constant pressure p_3 to a temperature T', indicted by point F. The adiabatic expansion in the motor is represented by FG and the subsequent heating of the air at atmospheric pressure by GA. The work obtained from the motor is represented by the area under the path $DFGA$, and the increase of work obtained by reheating is represented by the area $DFGE$.

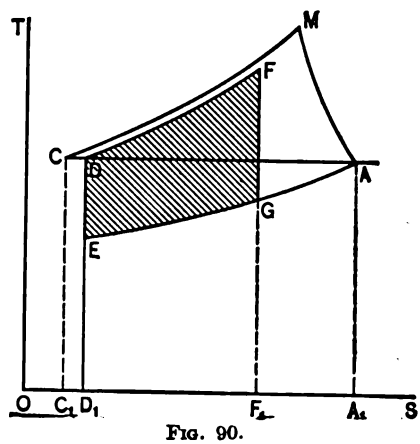


FIG. 90.

The work of the engine without reheating is given by the expression

$$W_e = \frac{k}{k-1} p_3 V_3 \left[1 - \left(\frac{p_1}{p_3}\right)^{\frac{k-1}{k}}\right], \qquad (1)$$

in which p_3, V_3 are the pressure and volume in the state indicated by point D. The heating of the air at the constant pressure p_3 increases the volume from V_3 to V_3', and the work of the engine with the reheated air is given by the expression

$$W_e' = \frac{k}{k-1} p_3 V_3' \left[1 - \left(\frac{p_1}{p_3}\right)^{\frac{k-1}{k}}\right]. \qquad (2)$$

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The ratio of the two is

$$\frac{W'}{W_e} = \frac{V_3'}{V_3} = \frac{T_f}{T_d}, \tag{3}$$

in which T_f and T_d denote, respectively, the absolute temperatures at points F and D.

For example, if the air is heated from 60° to 300°, the increase in the work of the motor is

$$\frac{760 - 520}{520} = 0.46, \text{ or } 46 \text{ per cent.}$$

Experiments on the use of reheated air have been made at the Engineering Experiment Station of the University of Illinois. These indicate that the heat required per indicated horsepower gained is 8,000 to 11,000 B. t. u. Thus one horspower is produced by a consumption of somewhat less than one pound of coal, a consumption considerably smaller than is attained by the best steam engines or even most internal combustion engines.

162. Effect of Clearance.—An actual compressor must have clearance, and the air remaining in the clearance space expands on the return stroke of the piston thus partially filling the cylinder and reducing the volume of the external air taken in during the stroke. In Fig. 91, curve CD represents the expansion of the air in the clearance space. The volume displaced by the piston is represented by the length V_p, the clearance volume by V_c, and the volume of air entering per stroke by V_1. To determine the relation between V_p and V_1, we have

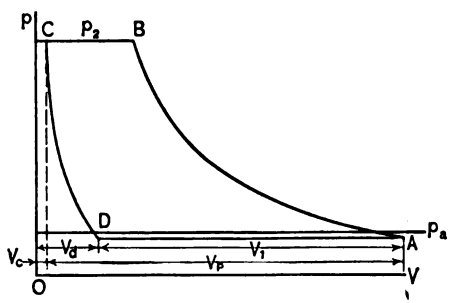


Fig. 91.

$$V_1 = V_p + V_c - V_d \tag{1}$$

and

$$V_d = V_c \left(\frac{p_2}{p_1}\right)^{\frac{1}{n}}, \tag{2}$$

in which n is the exponent of the polytropic curve CD.

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Take the ratio $\frac{V_c}{V_p} = m$; then (1) becomes

$$V_1 = V_p + mV_p - mV_p \left(\frac{p_2}{p_1}\right)^{\frac{1}{n}}$$

$$= V_p \left[1 + m - m \left(\frac{p_2}{p_1}\right)^{\frac{1}{n}}\right]. \quad (3)$$

The term in the bracket may be called the *clearance factor.*

If the value of n for the curve CD is the same as for the compression AB, the work of compression per stroke is given by the same expression as in the case of the compressor without clearance. The air in the clearance space acts like a spring, storing and giving back energy, and leaving the work of compression unaffected.

163. Volumetric Efficiency.—The pressure p_1 of the air entering the cylinder, that is, the pressure indicated by the suction line DA, Fig. 91, is somewhat lower than p_a, the pressure of the atmosphere. If M denotes the weight of air entering the cylinder, then

$$p_1 V_1 = MBT_1.$$

The volume of this weight M at atmospheric pressure is V_a given by the equation

$$p_a V_a = MBT_a.$$

The passage of the air through the admission valve with the drop in pressure from p_a to p_1 is a throttling process, and consequently for air the temperature remains practically constant. Hence $T_1 = T_a$, and

$$p_1 V_1 = p_a V_a. \quad (1)$$

The ratio $V_a : V_p$ of the free air actually taken into the compressor to the volume displaced by the piston is called the **volumetric efficiency** of the compressor. Denoting this efficiency by η_v, we have

$$\eta_v = \frac{V_a}{V_p} = \frac{V_1 \frac{p_1}{p_a}}{\frac{V_1}{1 + m - m\left(\frac{p_2}{p_1}\right)^{\frac{1}{n}}}} = \frac{p_1}{p_a}\left[1 + m - m \left(\frac{p_2}{p_1}\right)^{\frac{1}{n}}\right]. \quad (2)$$

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The value of η_v given by (2) may be reduced by leakage around the piston and through the valves.

It is evident that the efficiency η_v is smaller the higher the pressure p_2; hence the reduction of the pressure ratio by compounding gives the compound compressor a higher volumetric efficiency than the single stage compressor.

164. Calculation of an Air Compressor.—The volume of the compressor cylinder required for a given service is readily calculated. Let V_a denote the volume of free air (that is, air at atmospheric pressure) to be compressed per minute, and N the number of revolutions per minute. Then the volume V_1 at the pressure p_1 is

$$V_1 = \frac{p_a}{p_1} V_a, \tag{1}$$

and the displacement volume V_p per minute is given by (3), Art. 162. Therefore the volume per stroke, or the cylinder volume, is

$$V_c = \frac{V_p}{2N}. \tag{2}$$

Observe that the cylinder size is based on the volume V_p, but the power required is based on the volume V_1.

EXAMPLE. An air compressor is required to compress 3500 cu. ft. of free air per minute to a pressure of 120 lb. per sq. in. Required the cylinder dimensions and the horsepower required to drive the compressor.

The exponent n for both compression and expansion will be taken as $1.33 = \frac{4}{3}$; the clearance ratio m as 0.025; and the pressure p_1 at the beginning of compression as 13.8 lb. per sq. in.

We have then

$$V_1 = 3500 \times \frac{14.7}{13.8} = 3728 \text{ cu. ft.}$$

The clearance factor is

$$1 + 0.025 - 0.025\left(\frac{120}{13.8}\right)^{\frac{3}{4}} = 0.8984,$$

and the displacement volume is

$$V_p = 3728 \div 0.8984 = 4150 \text{ cu. ft.}$$

Taking $N = 85$ r.p.m.

$$V_c = \frac{4150}{2 \times 85} = 24.41 \text{ cu. ft.}$$

The piston diameter and stroke must be so adjusted as to give this volume, 24.41 cu. ft. Let the stroke be taken as 4 ft.; then the effective piston area is $24.41 \times 144 \div 4 = 879$ sq. in. The piston rod cuts out 10 to 15 sq. in.;

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hence the gross area should be, say, 894 sq. in., and the corresponding diameter is 33¾ in.

The work per minute is

$$W = \frac{n}{n-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}\right];$$

hence the horsepower required is

$$\frac{4 \times 144 \times 13.8 \times 3728}{33{,}000}\left[1 - \left(\frac{120}{13.8}\right)^{\frac{1}{4}}\right] = 644.$$

With 15 per cent. loss between the steam engine and compressor, the horsepower developed in the steam cylinder should be

$$644 \div 0.85 = 758.$$

For the compression pressure required, 120 lb. per sq. in., a compound compressor would effect a considerable saving in horsepower. The intermediate pressure should be

$$p' = \sqrt{p_1 p_2} = \sqrt{13.8 \times 120} = 40.7 \text{ lb.}$$

There is necessarily a drop in pressure as the air passes through the intercooler. Taking this drop as 1 lb., we may take 41 lb. as the terminal pressure in the low-pressure cylinder, and 40 lb. as the initial pressure in the high-pressure cylinder. The clearance factor for the low-pressure cylinder is

$$1 + 0.025 - 0.025\left(\frac{41}{13.8}\right)^{\frac{1}{4}} = 0.9684$$

and that for the high-pressure cylinder is practically the same, since the pressure ratios are nearly equal. The required displacement volume per minute is $3728 \div 0.9684 = 3850$ cu. ft. and the cylinder volume is $3850 \div 170 = 22.65$ cu. ft. With a stroke of 4 ft. the net piston area is 815.4 sq. in., which may be increased to 828 sq. in. to account for the area cut out by the piston rod. The corresponding piston diameter is 32½ in.

It is assumed that the air passing through the intercooler has its temperature reduced to the initial temperature of the air entering the low pressure cylinder. Hence the several volumes, V_1, V_p, and V_c for the high-pressure cylinder are equal to the same volumes for the low-pressure cylinder multiplied by the pressure ratio 13.8 : 40. The high-pressure cylinder volume is therefore

$$22.65 \times \frac{13.8}{40} = 7.847 \text{ cu. ft.}$$

and with the same stroke, 4 ft., the net piston area is 281.3 sq. in. Allowing, for the piston rod, the cylinder diameter is 19⅜ in.

The horsepower of the low-pressure cylinder is

$$\frac{4 \times 144 \times 13.8 \times 3728}{33{,}000}\left[\left(\frac{41}{13.8}\right)^{\frac{1}{4}} - 1\right] = 281;$$

that of the high-pressure cylinder is

$$\frac{4 \times 144 \times 13.8 \times 3728}{33{,}000}\left[\left(\frac{120}{40}\right)^{\frac{1}{4}} - 1\right] = 284.$$

The total horsepower is $281 + 284 = 565$, which is about 12 per cent. smaller than was required for the single stage compressor.

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165. Temperature after Compression.—The equation of the compression curve being pv^n = const., the relation between the pressures p_1 and p_2 and the absolute temperatures T_1 and T_2 is

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}, \tag{1}$$

from which T_2 may be determined when T_1 is known. Thus in the example of the preceding article, if the initial temperature is 70° F., the temperature at the end of the single-stage compression is given by the equation

$$T_2 = (70 + 459.6)\left(\frac{120}{13.8}\right)^{\frac{1}{4}} = 909.5$$

or $t_2 = 449°$ F., nearly. In the case of the compound compression, the temperature after the first stage compression is

$$T_2 = 529.6\left(\frac{41}{13.8}\right)^{\frac{1}{4}} = 659.3,$$

or $t_2 = 235.7°$ F.

166. Heat Rejected to Jackets and Intercooler.—Referring to Fig. 89, the area A_1APP_1 represents the heat rejected to the water in the jacket of the first cylinder during the compression phase, and area P_1PQQ_1 represents the heat rejected in cooling the air from the temperature T_2 to the initial temperature T_1. A little of this latter may be rejected to the jacket-water during the expulsion of the air, but the major part is given up to the water circulating in the intercooler. According to Art. 159, the heat given up during compression is

$$Q_j = Mc_v\frac{k-n}{n-1}(t_2 - t_1) \tag{1}$$

and the heat given up during the cooling at constant pressure is

$$Q_i = Mc_p(t_2 - t_1). \tag{2}$$

In these expressions the sign has been changed so as to give the positive sign to heat rejected. The sum $Q_j + Q_i$ is the heat equivalent of the work of the compressor on M lb. of air. The ratio $Q_j : Q_i$ is

$$\frac{Q_j}{Q_i} = \frac{c_v}{c_p}\frac{k-n}{k-1} = \frac{k-n}{k(n-1)}. \tag{3}$$

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From this equation and the equation

$$Q_j + Q_i = AW$$

the following are obtained:

$$Q_j = AW \frac{k - n}{n(k - 1)}, \tag{4}$$

$$Q_i = AW \frac{k(n - 1)}{n(k - 1)}. \tag{5}$$

If the compression is adiabatic $n = k$, $Q_j = 0$, and $Q_i = AW$; if it is isothermal, $n = 1$, $Q_j = AW$, and $Q_i = 0$.

EXAMPLE. Taking the results of the example of Art. 164, find the heat rejected per minute to the water in the jacket of the low-pressure cylinder and to the water in the intercooler.

Since 1 h.p.-min. = 42.44 B. t. u., the heat equivalent of the work of the low-pressure compressor per minute is

$$AW = 281 \times 42.44 = 11{,}926 \text{ B. t. u.}$$

With $n = \frac{1}{4}$, $k = 1.4$, the fractions in (4) and (5) have the values $\frac{1}{8}$ and $\frac{7}{8}$ respectively; hence

$$Q_j = 11926 \times \tfrac{1}{8} = 1{,}491 \text{ B. t. u.}$$
$$Q_i = 11926 \times \tfrac{7}{8} = 10{,}435 \text{ B. t. u.}$$

These figures do not give precisely the heats given to the jacket and intercooler, respectively, since a small part of Q_i is given up to the jacket during the expulsion of the air from the cylinder. They may, however, be used as the basis for calculating the water required for cooling purposes.

167. Compressed Air Engines.—Engines for using compressed air as a medium do not differ essentially from steam engines; in fact, a steam engine may be used without change. If the expansion is complete, the cycle of the engine is that of the compressor traversed in the opposite sense, and the power delivered by the motor may be calculated by the formula for the power of the compressor. If the expansion is not complete, the mean effective pressure of the indicative diagram may be found by integrating the areas under the individual curves. It may be assumed that the curves are polytropic, $pv^n = \text{const.}$ Since there is some transfer of heat from cylinder walls to air, and vice versa, the value of n will usually be slightly less than 1.4, the adiabatic exponent.

The consumption of air may be found from the volume, pressure, and temperature at cut-off (or release) and compression, respectively.

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If the air is not preheated before entering the engine cylinder, the temperature at the end of expansion is necesarily low; thus, if air enters at 70 ° and expands adiabatically from 70 lb. to 16 lb. per sq. in., the final temperature is

$$T_2 = (70 + 459.6)\left(\frac{16}{70}\right)^{\frac{1.4-1}{1.4}} = 374.4$$

or $t_2 = -95.2°\text{F}$. As the temperature falls the water vapor present in the air is partly condensed and freezes. Aside from the increase of efficiency, preheating has the advantage of obviating the practical difficulties arising from the accumulation of ice or frost in the cylinder and valves.

168. Transmission of Power by Compressed Air.—The transmission system includes: (1) the air compressors usually driven by steam engines; (2) the pipe; (3) the air engines. Let P denote the horsepower developed in the steam cylinders, then ηP is the power delivered by the engines. The coefficient η is the product of the five efficiencies discussed in the following paragraphs.

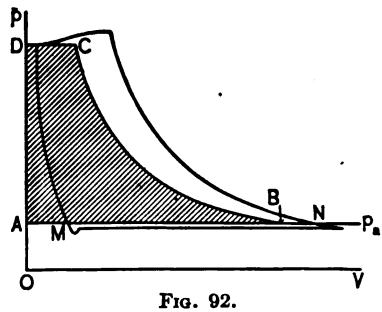


FIG. 92.

1. There are mechanical losses due to the friction in the engine and compressor. The ratio of the work done on the air to the work done in the steam cylinder is the mechanical efficiency of the combined engine and compressor, and may be denoted by η_1.

2. An arbitrary cylinder efficiency for the compressor is denoted by η_2. This efficiency is obtained by taking the ratio of the work of compressing *isothermally* V_a cu. ft. of free air from pressure p_a to pressure p_2 to the work actually done on the air. Referring to Fig. 92, let the atmospheric line $p_a = 14.7$ lb. be drawn cutting the indicator diagram of the compressor in the points M and N. Then the segment MN represents the volume V_a of free air taken into the compressor. Taking $AB = MN$, the ideal diagram $ABCD$ is constructed with the curve BC an equilateral hyperbola representing isothermal compression. The efficiency η_2 is then the ratio of the area $ABCD$ to the area of the actual diagram.

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The work represented by the area $ABCD$ is given by the equation

$$W = p_a V_a \log_e \frac{p_2}{p_a}. \tag{1}$$

3. If the air entered the engine at the pressure p_2 and expanded isothermally to the pressure p_a, equation (1) would give also the work delivered by the engine. The work actually delivered is considerably less for two reasons: There is a drop of pressure in the pipe so that the air enters the engine at a pressure p_3 somewhat lower than p_2. See Fig. 86. Then the expansion in the engine is not isothermal but more nearly adiabatic. Referring to Fig. 86, $HCAF$ is the indicator diagram of the engine without drop of pressure and with isothermal expansion, and $GDEF$ is the ideal diagram with adiabatic expansion from p_3 to p_a. The ratio of these areas may be regarded as a third efficiency η_3. An expression for the work represented by the diagram $GDEF$ is given by (5), Art. 158, namely

$$W_e = \frac{k}{k-1} p_a V_a \left[1 - \left(\frac{p_a}{p_3}\right)^{\frac{k-1}{k}}\right]; \tag{2}$$

hence the coefficient η_3 is given by the expression

$$\eta_3 = \frac{\frac{k}{k-1} p_a V_a \left[1 - \left(\frac{p_a}{p_3}\right)^{\frac{k-1}{k}}\right]}{p_a V_a \log_e \frac{p_2}{p_a}} = \frac{k}{k-1} \frac{1 - \left(\frac{p_a}{p_3}\right)^{\frac{k-1}{k}}}{\log_e \frac{p_2}{p_a}}. \tag{3}$$

4. Because of various imperfections, as incomplete expansion, wiredrawing, etc., the indicated power of the engine is less than that calculated from (2). The ratio of the two is a fourth efficiency η_4.

5. Finally, the indicated horsepower of the engine multiplied by the mechanical efficiency η_5 gives the horsepower delivered at the engine shaft.

The product $\eta_1 \cdot \eta_2 \cdot \eta_3 \cdot \eta_4 \cdot \eta_5$ gives the overall efficiency η.

For a modern single-stage compressor, we may take $\eta_1 = 0.85$ to 0.90, and $\eta_2 = 0.70$ to 0.80; for a two-stage compressor, $\eta_1 = 0.80$ to 0.90, and $\eta_2 = 0.80$ to 0.88. The coefficient η_3 is a function of the three pressures involved and may be calculated from equation (3). It decreases as the length of the pipe and the

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resulting drop of pressure $p_2 - p_3$ increase. Under favorable conditions the efficiency η_4 should be 0.80 to 0.90, and the efficiency η_5, 0.85 to 0.92.

EXAMPLE. Consider a compressed-air transmission system operating under the following conditions. Indicated horsepower of steam engines, 5000; length of pipe, 5 miles; air compressed to a pressure of 180 lb. per sq. in. An estimate of the work delivered by the air engine is required.

For a pressure of 180 lb. a two-stage compressor should be used. Taking $\eta_1 = 0.85$ and $\eta_2 = 0.84$, the horsepower corresponding to the ideal isothermal compression is

$$5000 \times 0.85 \times 0.84 = 3570.$$

This power is equivalent to $3570 \times 550 = 1{,}963{,}500$ ft.-lb. per sec. If V_a denotes the volume of free air entering the compressor per second, the work per second is given by the expression

$$W = p_a V_a \log_e \frac{p_2}{p_a};$$

hence we have

$$144 \times 14.7 \times V_a \log_e \frac{180}{14.7} = 1{,}963{,}500,$$

and

$$V_a = 370.4 \text{ cu. ft. per sec.}$$

The weight flowing per second, taking 70° F. as the temperature of the free air is 27.75 lb. These figures are required in the determination of the diameter of the pipe.

Assume that a drop of pressure of 30 lb. is required to carry the air through the pipe without using an excessive diameter. Then $p_2 = 180$ lb. and $p_3 = 150$ lb. From (3) the efficiency η_3 is

$$\frac{1.4}{1.4 - 1} \frac{1 - \left(\frac{14.7}{150}\right)^{\frac{0.4}{1.4}}}{\log_e \frac{180}{14.7}} = 0.678.$$

The horsepower corresponding to the ideal engine cycle is therefore $3570 \times 0.678 = 2420$. With $\eta_4 = 0.90$ and $\eta_5 = 0.90$, the horsepower finally delivered is $2420 \times 0.90 \times 0.90 = 1960$. It is reasonable to assume therefore that under the conditions stated an overall efficiency of nearly 0.40 may be attained.

Suppose now that the air is heated from 70° to 350° before entering the engine. The horsepower delivered, assuming that η_4 and η_5 remain unchanged, becomes

$$1960 \times \frac{350 + 459.6}{70 + 459.6} = 2996,$$

and the overall efficiency, not taking account of the fuel required for reheating the air, is raised to 0.60 nearly.

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EXERCISES

1. Find the power required to compress 1600 cu. ft. of free air per minute from 14.2 lb. to 85 lb. in a single-stage compressor. Assume that $n = 1.33$.
Ans. 231.2 h.p.

2. The air at the beginning of compression has a temperature of 77° F. Find the temperature at the end of compression. Ans. 377° F.

3. Find the heat rejected to the jacket water per minute during compression. Ans. 1291 B. t. u.

4. Calculate the power required assuming adiabatic compression and find the saving of power effected by the water jacket. Ans. 8.5 h.p. saved.

5. The clearance volume is 2 per cent. of the displacement volume. Find the cylinder volume if the compressor makes 90 revolutions per minute.
Ans. 9.76 cu. ft.

6. A three-stage compressor is used to compress air to a pressure of 750 lb. per sq. in. The capacity is 900 cu. ft. of free air per minute. The exponent n is 1.35, and the drop of pressure through the intercoolers may be neglected. Take the initial pressure as 14 lb. and calculate the power required. Ans. 274.4 h.p.

7. Find approximately the heat per minute rejected to each water jacket and to each intercooler.

8. Air arrives at the air-engine at a temperature of 65° F. Find the increase of power effected by heating the air to 415° F.
Ans. 66.7 per cent.

9. The cycle *AMCDEA*, Fig. 87, represents on the Ts-plane the various processes in the transmission of power by compressed air. Express the efficiencies η_2 and η_3 (Art. 168) in terms of areas shown in this figure.

10. In a transmission system the indicated horsepower of the steam engine is 1600 and the efficiencies η_1, η_2 are, respectively, 0.85 and 0.88. The air is compressed to 165 lb. Find (*a*) the ideal horsepower corresponding to isothermal compression from p_a to p_2; (*b*) the volume V_a of free air per minute entering the compressor. Ans. (*b*) 7716 cu. ft.

11. In the pipe the drop of pressure is 15 lb. Find the efficiency η_3.
Ans. 0.702

12. Take $\eta_4 = 0.90$ and $\eta_5 = 0.88$. Find the overall efficiency of the power transmission. Ans. 0.416

13. The clearance of an air compressor is 2.2 per cent. of the piston displacement and the initial and final pressures are respectively 14.1 lb. and 65 lb. Find (*a*) the clearance factor, and (*b*) the volumetric efficiency. $n = 1.3$.

14. In the preceding example find the volumetric efficiency with a final pressure of 140 lb.

15. An air compressor with a cylinder 18 in. by 24 in. is double-acting and is driven at a speed of 90 rev. per min. Clearance is 2 per cent. of piston displacement; $p_1 = 14.4$ lb. and $p_2 = 67$ lb. Find (*a*) the capacity of the compressor in cubic feet of free air per minute; (*b*) the indicated horsepower of the steam engine driving the compressor with $\eta_1 = 0.85$. Take $n = \frac{1}{3}$. Ans. (*a*) 795 cu. ft.; (*b*) 112.5 h.p.

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16. From equations (5) and (6), Art. 160, the following general equation may be deduced.

$$W_c = \frac{mn}{n-1} p_1 V_1 \left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{mn}}\right],$$

in which m denotes the number of stages. Take $p_1 = 14.7$, $p_2 = 1000$, $n = 1.3$ and calculate values of the variable factor $\frac{mn}{n-1}\left[1 - \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{mn}}\right]$ for $m = 5, 10, 20, 50, 100$. Show that as m is increased the value of this factor approaches $\log_e \frac{p_2}{p_1}$. Interpret this result.

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CHAPTER XIV

REFRIGERATION

169. Production of Cold.—In the general discussion of the cycles of heat motors it was pointed out that if the cycle be reversed the result is a refrigerating machine, in which the medium takes heat from the cold body and rejects heat to a body of higher temperature. This principle has been utilized in the construction of the compression refrigerating machine, which is so extensively used in various industries for the maintenance of low temperatures.

The object sought in "refrigeration" or the "production of cold" is the maintenance of the temperature of a body at a point lower than the temperature of surrounding bodies. Thus the rooms of a cold-storage warehouse may be kept at 20° to 40° F.; in ice-making the brine surrounding the cans of water must be kept at a temperature somewhat below 32° F. However well insulated the cold body may be, heat flows into it from the surroundings at higher temperature; hence the permanent maintenance of the low temperature implies the continuous removal of heat. The heat taken from the cold body must be rejected to some other body at a higher temperature. This second system is nearly always water; the medium after compression is put in contact with water, which absorbs the heat taken from the cold body and also additional heat, the equivalent of the external work required to drive the machine.

170. Refrigeration Cycles.—In the investigation of the refrigeration process, we have two temperatures of first importance; and these are fixed by the conditions of operation. (1) The temperature of the cold body, which is determined by the character of the service; thus for ice-making the temperature must lie considerably below 32° F., while for cold storage it may be 30° or 40° F. (2) The temperature of the water available for the absorption of heat.

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Let the absolute temperatures of the cold body and of the water be denoted by T_1 and T_2, respectively, and let these be represented on the Ts-plane by the horizontal lines T_1T_1 and T_2T_2, Fig. 93. The process of absorbing heat from the cold body is represented by a curve DA, Fig. 93(a), which must throughout lie below T_1. The medium is compressed adiabatically, as indicated by AB, and the rejection of heat to the water is represented by curve BC, which must therefore lie above T_2 throughout its length. By the adiabatic expansion CD the medium is returned to its initial state.

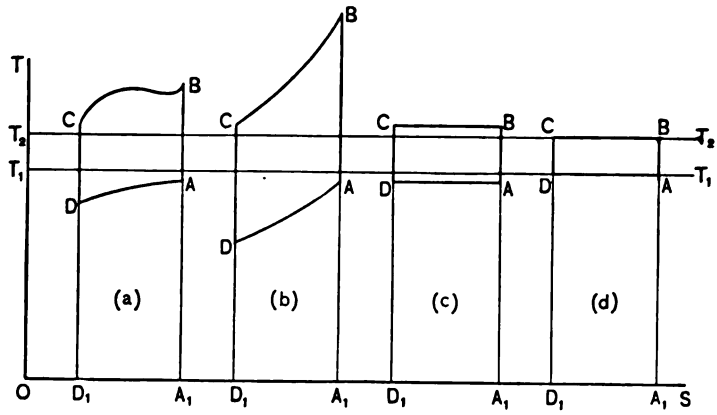


FIG. 93.

So far as the successful operation of a refrigerating machine is concerned, the only restriction on the processes DA and BC is the one indicated, namely, that DA shall lie wholly below T_1 and BC above T_2. In practice, however, the construction of the refrigerating machine requires that the medium remain at practically constant pressure during the changes DA and BC. If the medium is a gas, as air, the cycle has the form shown at (b); if it is a vapor mixture the lines of constant pressure are also lines of constant temperature and the cycle takes the form of the Carnot rectangle, shown at (c).

In each cycle the area D_1DAA_1 represents the heat taken from the cold body, that is, the useful effect, and the area $ABCD$ represents the work required. It is evident that the ratio of the heat removed to the work supplied is considerably greater

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for the vapor cycle than for the gas cycle. From the point of view of economy, a gas is a poor medium for a refrigerating machine.

171. Coefficient of Performance.—The refrigerating machine absorbs the heat Q_1 from the cold body, receives the work W from an external source, and rejects the heat

$$Q_2 = Q_1 + AW \tag{1}$$

to the warmer body. The useful effect is the heat Q_1, and the expense, which is to be made as small as possible, is the work W. It is evident that the larger Q_1 is compared with W, the more efficient is the refrigeration process. The ratio $\frac{Q_1}{AW}$ may therefore be taken as a measure of the efficiency of the machine. This ratio is called the *coefficient of performance*, and may be denoted by β.

With given temperatures T_1 and T_2, the smallest possible work is required when the cycle is a rectangle, as $ABCD$, Fig. 93 (*d*), with the isothermals coinciding with T_1 and T_2. The ideal coefficient of performance β_0 for this case is

$$\beta_0 = \frac{\text{area } D_1DAA_1}{\text{area } DABC} = \frac{T_1}{T_2 - T_1}. \tag{2}$$

The efficiency of a refrigerating machine may be defined as the ratio of its coefficient of performance to this ideal coefficient, that is

$$\eta = \frac{\beta}{\beta_0}. \tag{4}$$

The ideal coefficient of performance depends upon the temperature difference $T_2 - T_1$. The smaller the temperature difference can be made the larger the coefficient; hence the heat is absorbed from the cold body at as high a temperature as is permissible, and the temperature of the medium during rejection of heat is kept as low as possible.

The performance of a refrigerating machine may be expressed in terms of the heat removed from the cold body per horsepower-hour of work expended. Since one horsepower-hour is equivalent to 2546 B. t. u., the product 2546β gives the heat removed per hour per horsepower.

172. Units of Capacity.—The capacity of a refrigerating machine is measured by the heat removed in a unit of time. Thus

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1 B. t. u. per second or 1 B. t. u. per minute may be taken as a unit of capacity. The commercial unit usually employed is *the ton of ice per day*. By this expression is meant the removal in 24 hours of heat equivalent to that required to melt 2000 lb. of ice at 32° F. The latent heat of fusion of ice is 143⅓ B. t. u. per pound, which is 286,700 B. t. u. per ton. Dividing by 1440, the number of minutes in 24 hours, the ton of ice per day is equivalent to 199.03 B. t. u. per min. It is customary to use the round numbers 200 B. t. u. per min., 12,000 B. t. u. per hour, 288,000 B. t. u. per day.

For one horsepower the heat removed per hour is 2546β B. t. u.; hence, since one ton per day is equivalent to 12,000 B. t. u. per hour, the number of tons per horsepower is $\frac{2546\beta}{12{,}000} = 0.212\beta$, and the horsepower required to produce one ton of refrigeration is

$$\frac{12{,}000}{2546\beta} = \frac{4.71}{\beta}.$$

EXAMPLE. An ammonia refrigerating machine shows a coefficient of performance of 4.5. The heat removed per horsepower-hour is $2546 \times 4.5 = 11{,}460$ B. t. u., the capacity is $\frac{11{,}460}{12{,}000} = 0.955$ tons per horsepower.

173. The Air Refrigerating Machine.—The arrangement of the air machine is shown diagrammatically in Fig. 94. It has

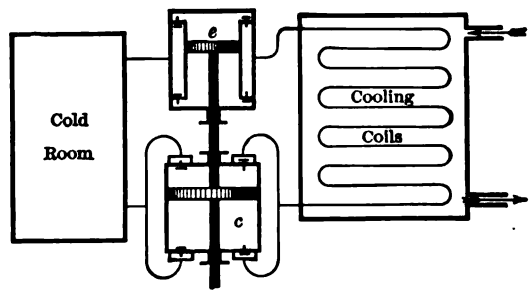


FIG. 94.

four essential organs, the compressor c, the expansion cylinder e, the cooling coils, in which heat is abstracted from the air by cold water, and the cold room. The operation of the machine may be studied in connection with the ideal TS- and pV-diagrams,

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Fig. 95 and 96. The air leaves the cold room in the state indicated by point A and enters the compressor c where it is compressed adiabatically as indicated by AB. It then passes into the cooling coils, about which cold water circulates, and is cooled at constant pressure, as indicated by BC. In the state C the air passes into the expansion cylinder e and is permitted to expand adiabatically down to the pressure in the cold room, *i.e.* atmospheric pressure. The final state is represented by point D. Finally the air absorbs heat from the cold room, and its temperature rises to the original value T_a. Referring to Fig. 96, the indicator diagram of the compressor is $ABFE$, while the

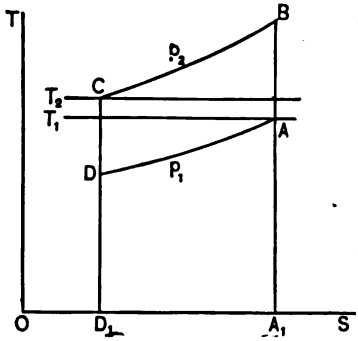


Fig. 95.

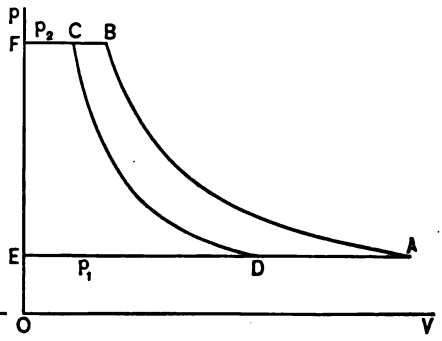


Fig. 96.

diagram $FCDE$ taken clockwise is the diagram of the expansion cylinder. The net work done on the air is, therefore, given by the diagram $ABCD$.

The Allen dense-air machine has a closed cycle and the air is always under a pressure much higher than that of the atmosphere. Thus the pressure p_1 is perhaps 40 to 60, and the upper pressure p_2 perhaps 200 lb. per square inch. The air, after expanding to the lower pressure, is led through coils immersed in brine and absorbs heat from the brine.

The ideal conditions outlined in the preceding paragraphs are modified in the actual machine. The compressor cylinder may be water jacketed so that the compression is not adiabatic; the expansion cylinder is, however, lagged so that the expansion is nearly adiabatic. Because of friction in the cooling coils there is a drop of pressure between the compressor and expansion

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cylinder. The indicator diagrams (without clearance) are as shown in Fig. 97. The compression curve AB has the equation pv^n = const., where n is less than 1.4, while the expansion curve CD is an adiabatic. The pressure drops from p_2 to p_3 in the cooler.

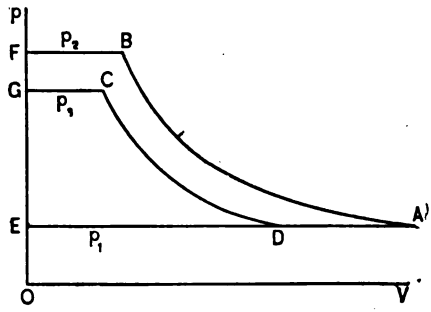


FIG. 97

174. Performance of the Air Machine.—The data required for the calculation are: the temperatures of the cold room and the cooling water, the refrigeration to be effected in tons per day, or in B. t. u. removed per minute, and the pressures.

The temperature T_a corresponding to the state A, Fig. 95, may be taken as the temperature of the cold chamber, and the temperature T_c is somewhat higher than the temperature of the cooling water. Having these temperatures, the temperatures T_b and T_d may be found from the equations

$$\frac{T_b}{T_a} = \left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}}, \qquad \frac{T_d}{T_c} = \left(\frac{p_1}{p_3}\right)^{\frac{k-1}{k}}. \tag{1}$$

Let Q_1 denote the heat abstracted from the cold room per minute and M the weight of air circulated per minute. The heat Q_1 is absorbed during the process DA, that is, at constant pressure; hence

$$Q_1 = Mc_p(T_A - T_D), \tag{2}$$

from which M may be calculated.

Let V_a and V_b denote, respectively, the volume of M lb. of air in the states A and B. Then the work of the compressor per minute, represented by the indicator diagram $ABFE$, is

$$W_c = \frac{n}{n-1}(p_1V_a - p_2V_b) = \frac{n}{n-1}MB(T_a - T_b). \tag{3}$$

This expression gives a negative result, since the work is done *on*

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the air. Similarly the work done in the expansion cylinder per minute, represented by the indicator diagram $GCDE$, is

$$W_e = \frac{k}{k-1}(p_2V_c - p_1V_d) = \frac{k}{k-1}MB(T_c - T_d). \quad (4)$$

The net work that must be furnished from an external source is

$$W = W_c + W_e,$$

and the coefficient of performance is the ratio $Q_1 : AW$.

The heat equivalent of the work W added to Q_1 gives Q_2, the heat discharged to the cooling water.

If the compressor makes N working strokes per minute the weight of air entering the cylinder per stroke is M/N; and the volume of this air in the state A is

$$V' = \frac{M}{N}\frac{BT_a}{p_1}. \quad (5)$$

Likewise the volume in the state D is

$$V'' = \frac{M}{N}\frac{BT_d}{p_1} = V'\frac{T_d}{T_a}. \quad (6)$$

Neglecting clearance, V' is the necessary volume displaced by the compressor piston, and V'' the volume of the expansion cylinder. To provide for clearance these volumes must be increased as indicated in Art. 162; and it is advisable to add 5 or 10 per cent. extra to take account of leakage, imperfect valve action, etc.

EXAMPLE. An air refrigerating machine is required to abstract 600 B. t. u. per min. from a cold room. The pressure in the cold room is 14.7 lb. per sq. in., the air is compressed according to the law $pv^{1.37} = \text{const.}$ to a pressure of 65 lb. per sq. in. and enters the expansion cylinder at a pressure of 55 lb. per sq. in. The temperature of the cold room is 36° F. and the air leaves the cooling coils at 80° F. The machine makes 120 working strokes per minute. Required the horsepower to drive the machine, and the cylinder volumes.

We have, $T_a = 495.6$, $T_c = 539.6$; and the temperatures T_b and T_d are to be found.

$$T_b = T_a\left(\frac{p_2}{p_1}\right)^{\frac{n-1}{n}} = 495.6\left(\frac{65}{14.7}\right)^{\frac{0.37}{1.37}} = 740.4.$$

$$T_d = T_c\left(\frac{p_1}{p_2}\right)^{\frac{k-1}{k}} = 539.6\left(\frac{14.7}{55}\right)^{\frac{0.4}{1.4}} = 370.1.$$

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The weight of air that must be circulated per minute is

$$M = \frac{600}{0.24(495.6 - 370.1)} = 19.91 \text{ lb.}$$

The work of the compressor per minute is

$$W_c = \frac{n}{n-1}(p_1V_a - p_2V_b) = \frac{n}{n-1}MB(T_a - T_b)$$
$$= \frac{1.37}{0.37} \times 19.91 \times 53.34 \times (495.6 - 740.4) = -963{,}120 \text{ ft. lb.}$$

Similarly, the work performed in the expansion cylinder is

$$W_e = \frac{k}{k-1}MB(T_c - T_d)$$
$$= \frac{1.4}{0.4} \times 19.91 \times 53.34 \times (539.6 - 370.1) = 630{,}360 \text{ ft. lb.}$$

The power required is therefore

$$963{,}120 - 630{,}360 = 332{,}760 \text{ ft.-lb. per min.,}$$

or 10.09 horsepower. The steam engine driving the machine should develop 14 or 15 indicated horsepower.

The heat equivalent of 332,760 ft. lb. is 427 B. t. u.; hence the heat rejected to the cooling water per minute is 600 + 427 = 1027 B. t. u.

The coefficient of performance is

$$\frac{Q_1}{AW} = \frac{600}{427} = 1.41$$

For the compressor volume we have from (5)

$$V' = \frac{19.91}{120}\frac{53.34 \times 495.6}{14.7 \times 144} = 2.072 \text{ cu. ft.}$$

and for the volume of the expansion cylinder

$$V'' = 2.072 \times \frac{370.1}{495.6} = 1.547 \text{ cu. ft.}$$

Let the clearance be 3 per cent. of the piston displacement for the compressor and 5 per cent. for the expansion cylinder; then the clearance factors are:

$$1 + 0.03 - 0.03\left(\frac{65}{1.47}\right)^{\frac{1}{1.4}} = 0.943$$

$$1 + 0.05 - 0.05\left(\frac{55}{14.7}\right)^{\frac{1}{1.4}} = 0.927$$

The required volumes are therefore

$$2.072 \div 0.943 = 2.197 \text{ cu. ft.}$$
$$1.547 \div 0.927 = 1.669 \text{ cu. ft.}$$

Let 10 per cent. be added to these values to provide for various imperfections; then the cylinder dimensions are:

Stroke, 21 in., diameter of compressor cylinder 16 in.,
diameter of expansion cylinder 13⅞ in.

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175. Vapor Compression Machines.—The essential organs of a compression machine using vapor as a medium are shown in Fig. 98. The action of the machine may be studied to advantage in connection with the Ts-diagram, Fig. 99. The medium is

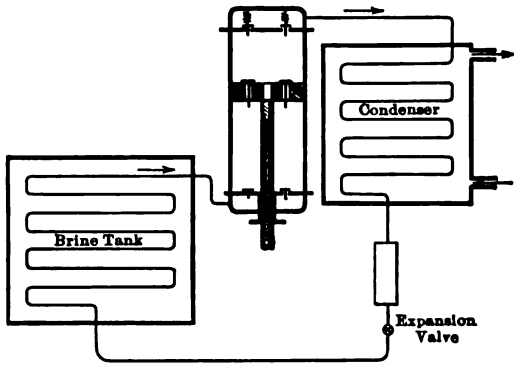


FIG. 98.

drawn into the compressor cylinder through the suction pipe from the coils in the brine tank. It may be assumed that the medium entering is in the saturated state at the temperature T_1, which may be taken equal to the temperature of the brine. This state is represented by point B. The vapor is compressed adiabatically to a final pressure p_2, which is determined by the upper temperature T_2 that may be obtained with the cooling water available. The adiabatic compression is represented by BC. The superheated vapor in the state C is discharged into the coils of the cooler or condenser, where heat is abstracted from it. The coils are surrounded by cold water which flows continuously. First the gas is cooled to the state of saturation; this process is represented by the curve CD, and the heat abstracted by the area C_1CDD_1. Then heat is further removed at

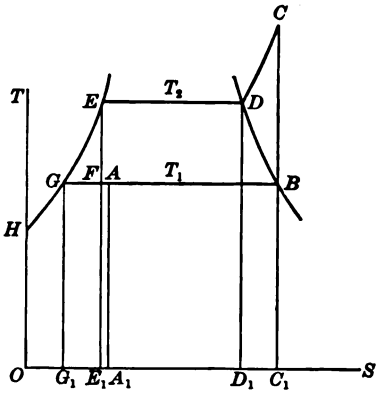


FIG. 99.

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the constant temperature T_2 (and pressure p_2) and the vapor condenses. At the end of the process, the medium is liquid and its state is represented by the point E on the liquid curve.

It should be noted that there are two parts of the fluid circuit: one including the discharge pipe and coils at the higher pressure p_2, and one including the brine coils and the suction pipe at the lower pressure p_1. These are separated by a valve called the **expansion valve.** The liquid in the state represented by point E is allowed to trickle through the valve into the region of lower pressure. The result of this irreversible free expansion is to bring the medium to a new state represented by point A. In this state the medium, which is chiefly liquid with a small percentage of vapor, passes into the coils in the brine tank or in the room to be cooled. The temperature of the brine being higher than that of the medium, heat is absorbed by the medium, and the liquid vaporizes at constant pressure. This process is represented by the line AB and the heat absorbed from the surrounding brine by the area A_1ABC_1.

The position of the point A is determined as follows: The passage of the liquid through the expansion valve is a case of throttling or wiredrawing of the character discussed in Art. 123. Hence, the thermal potential at A must be equal to the thermal potential at E, that is,

$$i'_2 = i'_1 + x_a r_1$$

Graphically, the area $OHGAA_1$ is equal to the area $OHEE_1$; or taking away the common area $OHGFE_1$, the rectangle E_1FAA_1 is equal to the triangle GEF.

Since the throttling process represented by EA is assumed to be adiabatic, the work that must be done on the medium is the difference between Q_1, the heat absorbed, and Q_2, the heat rejected to the condenser. We have then

$$\begin{aligned} Q_2 &= \text{area } C_1CDEE_1, \\ Q_1 &= \text{area } A_1ABC_1, \\ W &= \text{area } C_1CDEE_1 - \text{area } A_1ABC_1 \\ &= \text{area } BCDEE_1A_1AB \\ &= \text{area } BCDEGB. \end{aligned}$$

If the expansion valve be replaced by an expansion cylinder,

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permitting a reversible adiabatic expansion from p_2 to p_1, as indicated by the line EF, we have

$$Q_2 = \text{area } C_1CDEE_1,$$
$$Q_1 = \text{area } E_1FBC_1,$$
$$W = \text{area } BCDEFB.$$

The effect of using the expansion valve rather than the expansion cylinder is thus to decrease the heat removed by the area E_1FAA_1 and to increase the work done by an equal amount.

176. Vapors used in Refrigeration.—The three vapors that are used to any extent as refrigerating media are ammonia, sulphur dioxide, and carbon dioxide. The choice of vapor to be used depends chiefly upon two things: (1) The suction and discharge pressures that must be employed to give proper lower and upper temperatures T_1 and T_2. The lower temperature must be such as to keep the proper temperature in the brine or the space to be kept cool, while the upper temperature is fixed by the temperature of the cooling water available. (2) The volume of the medium required for a given amount of refrigeration. This determines the bulk of the machine.

If the upper temperature be taken as 68° F. ($T_2 = 528$) and the lower temperature at 14° F., the pressures and the volume ratios for the three vapors mentioned are about as follows:

	NH_3	SO_2	CO_2
Suction pressure, lb. per sq. in.....	41.7	14.7	380
Discharge pressure, lb. per sq. in.....	124.7	47.6	825
Volume, taking that of CO_2 as 1.....	4.4	12.0	1

It appears that carbon dioxide requires for proper working very high pressures, so high, in fact, as to be practically prohibitive except in machines of small size. With sulphur dioxide the pressures are low, but the necessary volume of medium is high, being nearly three times that required by ammonia and twelve times that required by carbon dioxide. With ammonia, the pressures are reasonable and the volume of medium is not excessive; hence from these considerations, ammonia is seen to be most advantageous.

With respect to economy, ammonia and sulphur dioxide are about equal. Carbon dioxide shows a somewhat smaller efficiency than the others under similar conditions because,

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on account of the small latent heat of carbon dioxide, the losses due to superheating and the use of the expansion valve are a larger per cent. of the total effect.

177. Calculation of the Vapor Compression System.—The cycle of the compression refrigeration machine transferred to the *is*-plane is shown in Fig. 100. The same letters in Fig. 99 and 100 denote the same states. The adiabatic compression is represented by BC, the point B lying on the saturation curve s'' at its intersection with the line p_1 = const. Line CE represents the cooling and condensation of the vapor at constant pressure p_2. The heat q_2 discharged to the cooling water per unit weight of medium is therefore the difference of thermal potential between states C and E; that is,

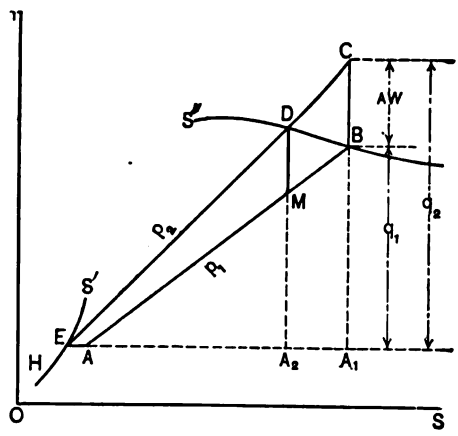


FIG. 100.

$$q_2 = i_c - i_e, \qquad (1)$$

and this heat is represented by the segment CA_1. Point E represents liquid at the condenser pressure p_2, point A represents the state of the medium after the passage through the expansion valve. According to the equation for a throttling process, $i_a = i_e$, therefore A lies at the intersection of a horizontal line through E with the line p_1 = const. The process AB is the vaporization in the brine coils, or in the cold room, during which heat q_1 is abstracted from the brine. Since the process is at constant pressure,

$$q_1 = i_b - i_a = i_b - i_e, \qquad (2)$$

and this heat is represented by the segment A_1B. From (1) and (2)

$$AW = q_2 - q_1 = i_c - i_b; \qquad (3)$$

that is, the work required in thermal units is the change of thermal potential during the adiabatic compression.

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The coefficient of performance is

$$\beta = \frac{q_1}{AW} = \frac{i_b - i_e}{i_c - i_b}. \tag{4}$$

The heat q_1 is absorbed by one pound of the medium; hence if Q_1 is the refrigeration required in B. t. u. per minute the weight M of the medium circulated per minute is

$$M = \frac{Q_1}{q_1} = \frac{Q_1}{i_b - i_e}, \tag{5}$$

the work required per minute is $JM(i_c - i_b)$, and the net horsepower required to drive the machine is

$$H = \frac{JM(i_c - i_b)}{33{,}000} = \frac{Q_1}{42.44}\frac{i_c - i_b}{i_b - i_e}. \tag{6}$$

Assuming the vapor entering the compressor to be dry and saturated, as indicated by point B, the volume of vapor entering the compressor per stroke is

$$V = \frac{Mv_1''}{N}, \tag{7}$$

in which v_1'' is the specific volume of vapor at the pressure p_1 and N the number of working strokes per minute. If the medium enters the compressor as a mixture of quality x, v_1'' is replaced by the product xv_1''. The cylinder volume thus calculated must be increased to provide for clearance and various imperfections.

In the preceding formulas the values of the thermal potential i for the states represented by the points B, C, and E are required. In the case of dry compression point B is assumed to lie on the saturation curve, hence i_b is the thermal potential of the saturated vapor at the pressure p_1. Since point E lies on the liquid curve, i_e is the thermal potential of the liquid at the condenser pressure p_2. At point C the pressure p_2 and the entropy, which is equal to the entropy at point B, are known. If a table of properties of the superheated vapor is available, the potential at C is readily determined from the known values of p and s.

EXAMPLE. An ammonia refrigerating machine is to have a capacity of 75 tons of ice in 24 hours; the temperature of the ammonia in the brine coils is 12° F., and the pressure in the condenser is 175 lb. per sq. in. The compressor is double-acting and makes 80 rev. per min. Required the horsepower and size of cylinder.

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From the table of saturated ammonia we have for saturated vapor at 12° F., $i_b = 541.7$ B. t. u., $s_b = 1.1495$. For liquid ammonia at a pressure of 175 lb. per sq. in., $i_c = 62.6$ B. t. u. From the table of superheated ammonia (or from a Mollier chart) we find for $p = 175$ and $s = 1.1495$, $i_e = 633.5$. Using these values in the preceding formulas, we find for the heat absorbed from the brine per pound of ammonia circulated

$$q_1 = i_b - i_c = 541.7 - 62.6 = 479.1 \text{ B. t. u.},$$

for the work per pound of ammonia

$$AW = i_e - i_b = 633.5 - 541.7 = 91.8 \text{ B. t. u.},$$

and for the coefficient of performance

$$\beta = 479.1 \div 91.8 = 5.22.$$

The heat abstracted per minute is $75 \times 200 = 15{,}000$ B. t. u., therefore the weight of ammonia circulated is

$$M = \frac{Q_1}{q_1} = \frac{15{,}000}{479.1} = 31.31 \text{ lb. per min.}$$

The work required per minute is

$$31.31 \times 91.8 \times 778 \text{ ft.-lb.}$$

and the horsepower is therefore

$$H = \frac{31.31 \times 91.8 \times 778}{33{,}000} = 67.76.$$

The steam engine driving the compressor should develop perhaps 80 or 85 h.p.

The specific volume v_1'' of the saturated ammonia at 12° F. is 7.02 cu. ft. per pound; hence the calculated cylinder volume is

$$V = \frac{31.31 \times 7.02}{160} = 1.374 \text{ cu. ft.}$$

Adding 15 per cent. to provide for clearance and various imperfections the required volume is 1.58 cu. ft. This volume is given by a diameter of 13 in. and a stroke of 20½ in.

178. Wet Compression.—When the vapor is taken into the compressor in the saturated state, as indicated by point B, Fig. 100, it is superheated by compression, and the effect is a loss of efficiency. The superheating may be avoided by taking the vapor into the compressor in the state represented by point M so that at the end of compression the state is represented by point D on the saturation curve. The quality at M is determined from the relation

$$s_d = s_2'' = s_1' + x\frac{r_1}{T_1}. \qquad (1)$$

The segment A_2M represents the heat q_1 abstracted from the brine per pound of medium and the segment MD represents the work required.

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EXAMPLE. Taking the data of the example of the preceding article, determine the coefficient of performance and power required when wet compression is employed.

For the state represented by point D we find $i_d = 558.4$ B. t. u., and $s_d = 1.0250$. To get the initial quality in the state M we have $1.0250 = -0.0438 + 1.1933x$, whence $x = 0.896$. The thermal potential for the state M is therefore $541.7 - 0.104 \times 562.8 = 483.2$ B. t. u.

$$q_1 = 483.2 - 62.6 = 420.6 \text{ B. t. u.}$$
$$AW = 558.4 - 483.2 = 75.2 \text{ B. t. u.}$$
$$\beta = 420.6 \div 75.2 = 5.59$$
$$M = 15{,}000 \div 420.6 = 35.66 \text{ lb.}$$
$$H = \frac{35.66 \times 75.2 \times 778}{33{,}000} = 63.23 \text{ horsepower.}$$

For the cylinder volume, we have

$$V = \frac{35.66 \times 7.02 \times 0.896}{160} = 1.401 \text{ cu. ft.}$$

Comparing the two cases, it is seen that with wet compression the horsepower required is about 7 per cent. less while the cylinder volume is slightly greater.

In a second method of wet compression the vapor enters the compressor in the saturated condition and liquid ammonia is injected above the piston throughout the compression stroke. The vaporization of the liquid absorbs heat and thus prevents superheating.

179. The Ammonia Absorption System.—Water has the capacity of absorbing certain vapors, especially ammonia. The weight of vapor absorbed per pound of water depends upon the temperature and pressure; thus at a pressure of 30 lb. per sq. in. 0.698 lb. of ammonia is absorbed at 80° F. and 0.158 lb. at 180° F. The absorption process is accompanied by a generation of heat. If, therefore, a solution of ammonia in water is heated some of the dissolved ammonia will be driven off.

These properties of ammonia solutions are the basis of the ammonia absorption system of refrigeration. The diagram, Fig. 101, shows the arrangement of such a system. The generator contains a concentrated solution of ammonia in water. Heat is applied to the solution, usually by means of a steam coil, and as a result, ammonia is separated from the water. This ammonia at high pressure and temperature passes to the condenser, where it rejects heat to the cooling water and is condensed, then through the expansion valve to the brine cooler, where it absorbs

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heat from the brine and is evaporated. The absorber contains a weak solution which is kept at low temperature by the circulation of cold water. The vapor from the brine coil is absorbed by this weak solution and the rate of absorption is sufficient to maintain the required low pressure in this part of the system. The heat of solution is removed by the circulation of cold water through the absorber.

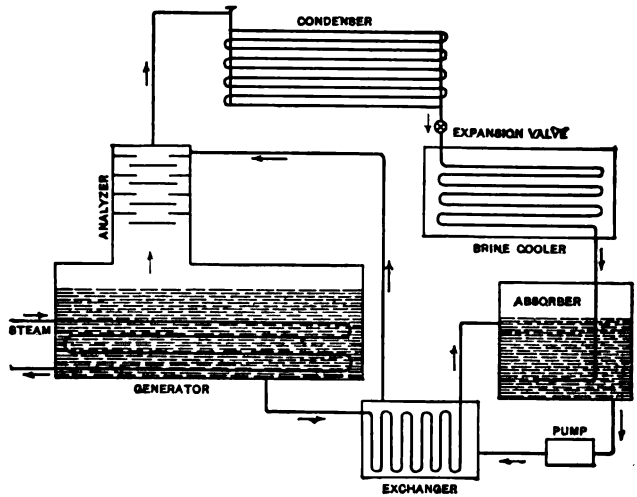


FIG. 101.

Between the generator and absorber there are three channels of communication. One is through the condenser, expansion valve, and brine coil, as just described; through this channel passes the ammonia that effects the refrigeration. The separation of the ammonia from the solution in the generator reduces the strength of that solution, while the absorption of ammonia in the absorber increases the strength of the weak solution. It is therefore necessary to interchange the two solutions. Weak liquor flows directly from the generator to the absorber, and strong liquor is taken from the absorber and by means of a pump is forced into the generator. From m lb. of strong solution let one pound of ammonia be driven off, leaving $m - 1$ lb. of weak liquor. The pound of ammonia passes through the condenser and brine, the $m - 1$ lb. of weak liquor flows to the

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absorber and again unites with the ammonia, forming m lb. of strong liquor, which is pumped back into the generator.

For the efficient operation of an absorption system certain auxiliary organs are required. The ammonia vapor driven from the strong solution is superheated and carries with it some water vapor. The *analyzer*, which forms the upper part of the generator contains a series of trays. The rich liquor from the pump is introduced into the top of the analyzer and thus comes in intimate contact with the vapor rising from the generator. The vapor is enriched in ammonia, the superheat is reduced and some of the water vapor is carried back to the generator. To reduce still farther the water content of the vapor a *rectifier* may be placed between the analyzer and condenser. In the rectifier the vapor is cooled by water, most of the water vapor is condensed and separated from the ammonia, and the water is returned to the generator.

The solution in the generator is necessarily at a higher temperature, about 270°–280°F., the solution in the absorber must be kept at a much lower temperature, say 130°–145°F. Hence the hot weak solution passing from generator to absorber must be cooled to the absorber temperature and the strong solution passing in the reverse direction must be heated to the temperature in the generator. By means of the *exchanger*, heat is imparted from the weak to the strong solution and thus the waste of heat is reduced.

180. Properties of Ammonia Solutions.—The concentration of the solution is the ratio of the weight of ammonia present to the weight of the solution; thus if 1 lb. of ammonia is contained in m lb. of the solution the concentration is $x = 1/m$. Suppose that the strong solution has a concentration x_1 and that by driving off 1 lb. of ammonia from n lb. of strong liquor the concentration is reduced to x_2. To determine the weight n, we have:

weight of ammonia in strong solution $= nx_1$,
weight of ammonia in weak solution $= (n - 1)x_2$,

therefore $$nx_1 - (n - 1)x_2 = 1,$$

or $$n = \frac{1 - x_2}{x_1 - x_2}. \qquad (1)$$

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For example, to reduce the concentration from 0.25 to 0.15 the weight of strong liquor required per pound of ammonia removed is $0.85 \div 0.10 = 8.5$ lb.

The weight of ammonia that can be absorbed by a pound of water depends upon the temperature and the pressure to which the solution is subjected. The experiments of Hilde Mollier on ammonia solution are represented approximately by the following equation;

$$\frac{T'}{T} = 0.466x + 0.656, \tag{2}$$

in which x denotes the concentration, T the absolute temperature of the solution, and T' the absolute temperature of saturated ammonia corresponding to the pressure on the solution. The formula is not valid for extremely small value of x or for values exceeding 0.50; but it is sufficiently exact for the concentrations used in practice.

When a weak solution of concentration x_2 absorbs *liquid* ammonia and thus raises the concentration to x_1 heat is developed, the amount of which depends on the mean concentration $\frac{1}{2}(x_1 + x_2)$. The experiments of H. Mollier on the heat of solution are represented fairly well by the equation

$$q_s = 345(1 - x) - 400x^2, \tag{3}$$

in which q_s denotes the heat generated per pound of ammonia absorbed, and x denotes the mean concentration $\frac{1}{2}(x_1 + x_2)$. The equation shows that q_s reduces to zero for $x = 0.59$; for all higher values of x the heat of solution is zero.

181. Conditions in the Absorber.—The ammonia enters the absorber from the brine cooler in the condition of saturated or slightly superheated vapor. There it is absorbed by the weak solution thus increasing the concentration. The upper limit of the temperature in the absorber for a required concentration x_1 is given by (2) of the preceding article. The cooling water passing through the absorber must remove a quantity of heat which is made up of three parts as follows: (1) The heat that must be abstracted from the entering gas to condense it to liquid at the temperature of the strong solution; (2) the heat of solution q_s; (3) the heat required to reduce the temperature of the weak solution to that of the strong solution

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leaving the absorber. The following example illustrates the calculation of the heat removed per pound of ammonia.

EXAMPLE. The pressure in the absorber is 30 lb. per sq. in. and the ammonia gas enters at a temperature of 5° F. The weak solution having a concentration 0.25 enters the absorber at a temperature of 100° F. By the absorption of the gas the concentration is increased to 0.35, and the strong solution leaves the absorber at a temperature of 80° F.

The temperature T' corresponding to a pressure of 30 lb. is 459.7; hence for $x_1 = 0.35$, we have from (2),

$$T = \frac{459.7}{0.466 \times 0.35 + 0.656} = 561.2, \text{ or } t = 101.6.$$

Since the temperature in the absorber is lower than 101.6, a concentration 0.35 is allowable.

From (1), $n = \frac{1 - 0.25}{0.35 - 0.25} = 7.5$ lb., the weight of strong solution per pound of ammonia. Therefore the weight of weak solution is 6.5 lb

At a pressure of 30 lb. and temperature of 5°, the value of i for superheated ammonia is 541.5 B. t. u.; and for liquid ammonia at 80° F., $i = 53.6$. The heat abstracted in the change of state may be taken as the difference, that is, 541.5 − 53.6 = 487.9 B. t. u. The heat of solution q_s is from (3) [$x = \frac{1}{2}(x_1 + x_2) = 0.30$]

$$345(1 - 0.30) - 400 \times 0.30^2 = 205.5 \text{ B. t. u.}$$

Hence the heat of solution of the gas is 487.9 + 205.5 = 693.4 B. t. u. The weak solution, 6.5 lb. per pound of ammonia, is cooled from 100° to 80°. The specific heat of ammonia solutions is not well known, but for this temperature range may be taken as 1.05. Then the heat removed is

$$6.5 \times 1.05 \times (100 - 80) = 136.5 \text{ B. t. u.}$$

The total heat leaving the absorber per pound of ammonia is therefore

$$693.4 + 136.5 = 829.9 \text{ B. t. u.}$$

182. Conditions in the Generator.—The processes occurring in the generator are the reverse of those in the absorber. Heat is supplied from an external source and is employed as follows: (1) To separate the liquid ammonia from the solution; (2) to vaporize the liquid and superheat the vapor; (3) to raise the temperature of the solution. In the following example the conditions correspond in some respects with those of the preceding example.

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EXAMPLE. The pressure in the generator is 150 lb. per sq. in. and the two concentrations are 0.25 and 0.35. Other conditions are to be determined and the heat required per pound of ammonia is required.

To find the minimum temperature for a 25-per cent solution, we have from (1)

$$T = \frac{78.5 + 459.6}{0.25 \times 0.466 + 0.656} = 696.6, \text{ or } t = 237° \text{ F.}$$

If steam at a pressure of 35 lb. is used its temperature is 259° and the generator temperature may be kept at 245°.

The weak solution leaving the generator gives up heat to the strong solution in the exchanger; however, the temperature of the strong solution entering the generator will probably not exceed 180°. The steam must supply heat to raise the temperature of the solution as well as the heat to drive the ammonia out of solution and vaporize it. It is assumed that the temperature of the superheated gas is 245°, the same as the temperature maintained in the generator. Actually it is somewhat lower.

The heat q_s to separate the ammonia from the solution is the same as before, that is, 205.5 B. t. u.

For ammonia liquid at 180°, i = 189.1 B. t. u.; for superheated vapor at 150 lb. and 245°, i = 660.1. Hence the heat required for this change of state is 660.1 − 189.1 = 471 B. t. u.

To raise the temperature of the 6.5 lb. of weak solution from 180° to 245°, taking the specific heat for this range as 1.15, the heat required is

$$6.5 \times 1.15 \times (245 - 180) = 370.9 \text{ B. t. u.}$$

Hence the total heat required by the generator per pound of ammonia circulated is

$$205.5 + 471 + 370.9 = 1047.4 \text{ B. t. u.}$$

In actual operation, the process is by no means as simple as that just outlined. Some of the water of the solution is driven off along with the ammonia, and there is an interchange of heat between the gas leaving the generator and the strong solution entering through the analyzer. An exact calculation of these effects is difficult.

EXERCISES

1. A temperature of 30° F. is to be maintained in a cold room and the temperature of the water available for absorption of heat is 58° F. (*a*) Find the ideal coefficient of performance. (*b*) Find the minimum horsepower required for the removal of 13,500 B. t. u. per minute.

2. A refrigerating machine has a coefficient of performance of 4.8, and 85 horsepower is expended in driving it. Find the capacity of the machine (*a*) in tons per day, (*b*) in B. t. u. per min.

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3. Find the coefficient of performance for a capacity of one ton of refrigeration per horsepower.

4. A dense-air refrigerating machine operates with pressures $p_1 = 60$ lb. and $p_2 = 220$ lb. Air enters the compressor at a temperature of 30° F. and the expansion cylinder at a temperature of 85° F. Assume that compression and expansion are adiabatic and that there is no drop of pressure between the cylinders. Find (*a*) coefficient of performance; (*b*) horsepower required for a capacity of 3000 B. t. u. per min.; (*c*) cylinder volumes for this capacity. Ans. (*b*) 29.4 h.p.

5. In the example of Art. 174, let the capacity be 850 B. t. u. per min. and the pressures 72 lb. and 60 lb., respectively; remaining data unchanged. Find the horsepower and the cylinder dimensions.

6. Ammonia enters the compressor in the state 1 specified below, is compressed to pressure p_2, and is cooled and condensed at that pressure. From the ammonia tables find the values of i in the initial state, at the end of compression, and of the liquid at pressure p_2; then from these find the coefficient of performance and the capacity in tons of refrigeration per horsepower.

	Initial State		p_2
(*a*)	$p_1 = 40$ lb.	$x_1 = 1$	160 lb.
(*b*)	$t_1 = 8°$ F.	$x_1 = 1$	175 lb.
(*c*)	$p_1 = 45$ lb.	$t_1 = 20°$	155 lb.
(*d*)	$p_1 = 32$ lb.	$x_1 = 0.90$	170 lb.

Ans. { (*b*) 4.90; 1.04 tons. (*d*) 5.32; 1.128 tons.

7. The pressure of ammonia entering the compressor from the brine cooler is 44 lb., and the pressure at the end of adiabatic compression is 180 lb. What must be the quality of the entering vapor in order that the state at the end of compression shall be that of saturated vapor? Ans. 0.879

8. With the data of Ex. 7, find the coefficient of performance. Find also horsepower required for a capacity of 400 tons of refrigeration.

Ans. 4.9; 384 h.p.

9. It has been assumed that the liquid just before its entrance to the expansion valve has a temperature t_2 corresponding to the pressure p_2 in the condenser. The point E, Fig. 100, represents the liquid in this state. By a proper arrangement of the cooling-water system the temperature may be reduced so that the state is represented by point H. Show that the effect is to increase the heat q_1 taken from the brine by the amount $i_e - i_h$, leaving the work unchanged.

10. In Ex. 6 suppose that in each case the liquid ammonia is cooled to 68° F. before passing through the expansion valve. Calculate the coefficient of performance and capacity, and compare with the original results.

Ans. { (*b*) 5.14 (*d*) 5.58

11. The following values of the refrigeration produced by ammonia in B. t. u. per h.p.-hour are taken from the Mechanical Engineers' Handbook, p. 349. Check several of the values.

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Condenser pressure, lb.	Temperature of liquid at expansion valve	Temperature of vapor in brine coil					
		30°	20°	10°	0°	−10°	−20°
150	50°	24,100	18,700	14,900	13,050	11,000	8,850
	70°	23,330	17,800	14,250	12,450	10,650	8,500
200	50°	17,800	14,400	12,200	10,650	9,150	7,550
	70°	17,000	13,800	11,600	10,100	8,750	7,250
	90°	16,100	13,000	11,150	9,650	8,250	6,850

12. An ammonia compression refrigerating machine working between the pressures $p_1 = 30$ lb. and $p_2 = 165$ lb. per sq. in. is to produce refrigeration equivalent to 60 tons of ice in 24 hours. The compressor is single-acting and makes 90 rev. per min. Find the net horsepower required, and the cylinder dimensions, after adding 15 per cent to the calculated volume.

13. With the data of Ex. 12 find horsepower and cylinder volume when wet compression is used.

14. In an ammonia absorption system the concentrations of the weak and strong solutions are, respectively, 0.20 and 0.32. Find (*a*) the weight of strong solution circulated per pound of ammonia; (*b*) the heat of solution of the ammonia liquid. Ans. (*a*) $6\frac{2}{3}$ lb.; (*b*) 227.3 B. t. u.

15. In the generator of an absorption system the temperature is maintained at 210° F. and the pressure at 170 lb. per sq. in. Find the corresponding concentration. Ans. 0.34.

16. The pressure in the absorber is 35 lb. per sq. in. and the ammonia entering from the brine cooler is saturated. The strong solution with a concentration $x_1 = 0.32$ leaves the absorber at a temperature of 110° F.; the entering weak solution has a temperature of 127° F. and its concentrations is 0.21. Assume the specific heat of the solution to be 1.05. Find the heat removed from the absorber per pound of ammonia circulated.

17. In a test of an ammonia absorption system the following data were obtained.

Steam pressure	62.4 lb. per sq. in.
Pressure in condenser	165.5 lb. per sq. in.
Pressure in brine cooler	38.4 lb. per sq. in.
Heat absorbed from brine per hour	481,260 B. t. u.
Steam used per hour	1,986 lb.

(*a*) Assume that the temperature of the ammonia liquid at the expansion valve is that correpsonding to the condenser pressure, and that dry saturated vapor leaves the brine cooler. Find the heat taken from the brine per pound of ammonia.

(*b*) Find the weight of ammonia circulated per hour.

(*c*) Find the heat abstracted from the brine per pound of steam used.

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(*d*) Assume that 6 per cent of the steam was used for driving the pump, the remainder in the generator. Find the heat delivered to the generator per pound of ammonia circulated.

Ans. (*a*) 482.7 B. t. u.; (*b*) 997 lb.
(*c*) 242.3 B. t. u.; (*c*) 1714 B. t. u.

18. For the absorption system of the preceding example let an ammonia compressor driven by a steam turbine be substituted. With the steam in the same initial condition (saturated at 62.4 lb.) and with a suitable condenser, the steam consumption per brake horsepower hour should not exceed 20 lb. It may be assumed that 85 per cent of the power developed by the turbine appears as the i. h. p. of the compressor, and the coefficient of performance, after deducting all losses, may be taken as 3.8. Show that the heat abstracted per pound of steam should exceed by about 70 per cent the result shown in Ex. 17.

19. It is recognized that the conditions under which the economy of an absorption system may equal or exceed that of a compression system are: (1) when exhaust steam is available and may be used in the generator; (2) when the suction pressure p_1 is low, as is required for ice-making and low-temperature refrigeration. Take appropriate data, for example, steam at a pressure of 16 lb., $p_1 = 15$ lb., calculate heat removed per pound of steam for each system, and verify the statement.

20. The performance of a refrigerating plant is frequently expressed in pounds of ice per pound of coal. The term pound of ice refers to the heat necessary to melt one pound of ice at 32°. Assuming an evaporation of 8 to 10 pounds of water per pound of coal find reasonable values for this coefficient of performance.

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CHAPTER XV

GASEOUS MIXTURES. COMBUSTION

183. The Problem of the Internal Combustion Engine.—In the technical applications involving the permanent gases that have been discussed—air compression, air refrigeration, etc.—the analysis was comparatively simple for two reasons. 1. The substance was a simple gas having well-known properties. 2. The temperature changes involved were comparatively small so that the assumption of a constant mean specific heat was justified.

There are, however, technical applications in which these conditions may not be assumed if a fairly exact analysis of the process is to be made. Consider, for example, the internal combustion engine. The medium employed is a mixture of gases rather than a simple gas, and, furthermore, its properties change during the cycle of operations. Thus before combustion the substance is a mixture of air and fuel gas; after combustion it is a mixture of products of combustion. The two mixtures usually have quite different properties. The range of temperature is large and the variation of specific heat with temperature may not be neglected. One of the processes, the combustion of the fuel, is a chemical change having certain thermal effects that must be taken into account. An accurate analysis of the cycle of the internal combustion engine involves therefore the following.

1. The properties of gaseous mixtures.
2. The effect of the variation of the specific heat.
3. The thermal effects of the combustion process.

The first two of these topics are treated rather fully in this chapter. The treatment of the combustion process is sufficient for most purposes; but it should be pointed out that a complete analysis of the complicated phenomena involved in gas reactions requires a knowledge of chemical equilibrium and kindred subjects that lie beyond the scope of this book.

184. Molecular Weights.—The atomic weights of the elements under immediate consideration are as follows.

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Element	Exact molecular weight	Approximate integral molecular weight
Oxygen	16	16
Hydrogen	1.008	1
Nitrogen	14.01	14
Carbon	12	12
Sulphur	32.07	32

The molecular weights of the diatomic gases H_2, N_2, and O_2, and those of the more important compounds are therefore as follows.

H_2 2	H_2O 18	SO_2 64	CH_4 16
O_2 32	CO 28	NH_3 17	C_2H_4 28
N_2 28	CO_2 44	NO 30	C_2H_6O 46

At the same pressure and temperature (thus, atmospheric pressure and 32° F.) the weights of equal volumes of gases are proportional to the molecular weights. If, for example, a given volume of oxygen weighs 32 lb. the same volume of hydrogen at the same pressure and temperature weighs 2 lb., and the same volume of CO_2 weighs 44 lb.

Calculations relating to gaseous mixtures are simplified by the introduction of a unit of weight called the *mol.* If m is used to denote the molecular weight of a gas, then 1 mol = m lb. or m grams, according as pounds or grams is taken as the unit. Thus

$$1 \text{ mol } O_2 = 32 \text{ lb. } O_2,$$
$$1 \text{ mol } NH_3 = 17 \text{ lb. } NH_3,$$
$$1 \text{ mol } CH_4 = 16 \text{ lb. } CH_4, \text{ etc.}$$

According to the relation between the volumes and weights of different gases, it appears that at a given pressure and temperature the volume of 1 mol is a definite fixed magnitude independent of the gas. At atmospheric pressure and 32° F. the weight of one cubic foot if oxygen is given as 0.08922 lb. Therefore, under these conditions, 1 lb. has a volume of $\frac{1}{0.08922}$ cu. ft. and 1 mol has a volume of $\frac{32}{0.08922} = 358.7$ cu. ft. This then is the volume of 1 mol of any gas at the assumed standard pressure and temperature.

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Frequently the properties of a gas are referred to a standard of temperature of 62° F. In this case the volume of 1 mol is

$$358.7 \times \frac{459.6 + 62}{459.6 + 32} = 380.6 \text{ cu. ft.}$$

185. The Universal Gas Constant.—The usual characteristic equation of a gas is

$$pv = BT, \tag{1}$$

in which v denotes the volume of one pound. Let v' denote the volume of one mol, that is, of m pounds of the gas; then $v' = mv$, and equation (1) may be written

$$pmv = mBT,$$

or

$$pv' = mBT. \tag{2}$$

Since the volume v' of one mol at a specified temperature and pressure is a definite constant, the product mB is a constant. The value of this constant depends on the system of units employed. Taking $p = 2116.3$ lb. per sq. ft. (atmospheric pressure) and $t = 32°$ F., the value of v' is 358.7. Hence we have

$$mB = \frac{2116.3 \times 358.7}{32 + 459.6} = 1544.$$

The constant product mB is denoted by R; and the gas equation referred to the mol as the unit of weight is

$$pv' = RT \tag{3}$$

The product AR is $\frac{1}{777.64} \times 1544 = 1.986$.

With the three constants, 358.7, 1544, and 1.986, expressions for certain properties of a gas in terms of the molecular weight m are readily obtained.

1. The volume of 1 pound at 32° F. and atmospheric pressure is

$$\frac{358.7}{m} \text{ cu. ft.}$$

2. The weight of 1 cubic foot under the same conditions is

$$\frac{m}{358.7} = 0.002788\, m \text{ lb.}$$

3. The difference $c_p - c_v$ of the specific heats is

$$c_p - c_v = AB = \frac{1.986}{m}.$$

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For example, take carbon monoxide CO, with $m = 28$

$$B = 1544 \div 28 = 55.14$$
$$c_p - c_v = 1.986 \div 28 = 0.0709.$$

Weight per cubic foot at 32° F. and atmospheric pressure,

$$0.002788 \times 28 = 0.07807 \text{ lb.}$$

The following table gives the constants of certain gases calculated from the preceding formulas.

Gas	Chemical symbol	Exact molecular weight m	Characteristic constant B	Difference of specific heats $c_p - c_v$	At atmospheric pressure and 32° F.	
					Weight of 1 cubic foot	Volume of 1 pound
Hydrogen	H_2	2.016	765.87	0.9849	0.005621	177.90
Oxygen	O_2	32.0	48.25	0.0621	0.08922	11.21
Nitrogen	N_2	28.02	55.10	0.0709	0.07812	12.80
Carbon dioxide	CO_2	44.0	35.09	0.0451	0.12268*	8.15
Carbon monoxide	CO	28.0	55.14	0.0709	0.07807	12.81
Methane	CH_4	16.032	96.31	0.1238	0.04470	22.37
Ethylene	C_2H_4	28.032	55.08	0.0708	0.07816	12.79
Air	.....	.....	53.34	0.0686	0.08071	12.39
Water vapor	H_2O	18.016	85.70**			

* According to the Smithsonian Physical Tables, 0.12341.

** Applicable at very low pressures, when water vapor follows closely the law of perfect gases.

186. Gas Mixtures.—Suppose that three different gases, having the same pressure p and temperature T, occupy the volumes V_1, V_2, V_3, Fig. 102. The weights of the three gases in pounds are respectively M_1, M_2, and M_3. If the partitions separating the gases be removed there will be a process of diffusion and ultimately each gas will be found distributed uniformly through the entire volume $V_1 + V_2 + V_3 = V$. Each gas expands from its original volume to the total volume V as if the other two gases were not present; consequently the pressure of the gas falls from the original value p to some new value. Since the temperature remains unchanged Boyle's law applies;

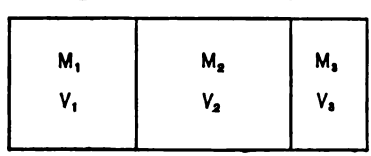


FIG. 102.

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hence denoting by p_1, p_2, p_3 the pressures of the three constituents in the mixture, we have

$$\left.\begin{aligned} pV_1 &= p_1V, \text{ or } p_1 = p\frac{V_1}{V}. \\ pV_2 &= p_2V, \quad p_2 = p\frac{V_2}{V}. \\ pV_3 &= p_3V, \quad p^3 = p\frac{V_3}{V}. \end{aligned}\right\} \tag{1}$$

From these equations two deductions are apparent:

1. $$p_1 : p_2 : p_3 = V_1 : V_2 : V_3, \tag{2}$$

that is, the partial pressures of the constituents in the mixture are proportional to partial volumes before mixing.

2. $$p_1 + p_2 + p_3 = p\frac{V_1 + V_2 + V_3}{V} = p. \tag{3}$$

The pressure of the mixture is the sum of the partial pressure of the constituents. This is **Dalton's law.**

Evidently the preceding discussion applies to any number n of gaseous constituents.

In the chemical analysis of a gaseous mixture as ordinarily made, the partial volumes V_1, V_2, etc. are obtained; therefore gas compositions are given in terms of volumes. For example, the composition of a producer gas is given as follows:

H_2	0.09
CO	0.24
CH_4	0.02
CO_2	0.06
N_2	0.59
	1.00

This composition may be interpreted in either of two ways: (1) If the gas is separated into its partial volumes, V_1, V_2, etc. each having the pressure and temperature of the mixture, then the H_2 has 9 per cent. of the total volume, the CO, 24 per cent, etc. (2) Because of the invariable relation between the volumes and weights in mols, the numbers of the volume composition are proportional to the number of mols in the several constituents. Thus 1 mol of the mixture is made up of 0.09 mol of H_2, 0.24

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mol of CO, etc. For many purposes this latter interpretation is very convenient.

The transformation from a volume to a weight composition is easily made. Thus for the producer gas in question, we have

	Weight in mols	Molecular weight m		Weight in lb.		Weight composition
H_2.....	0.09	2	2×0.09	0.18	$0.18 \div 26.38$	0.0068
CO.....	0.24	28	28×0.24	6.72	$6.72 \div 26.38$	0.2547
CH_4.....	0.02	16	16×0.02	0.32	$0.32 \div 26.38$	0.0121
CO_2.....	0.06	44	44×0.06	2.64	$2.64 \div 26.38$	0.1001
N_2.....	0.59	28	28×0.59	16.52	$16.52 \div 26.38$	0.6263
	1.00			26.38		1.0000

From this schedule it appears that 1 mol of the mixture weighs 26.38 lb. Strictly speaking a gaseous mixture cannot have a molecular weight; but the number 26.38 may be considered the *apparent* molecular weight, that is, the molecular weight of a hypothetical gas which at the same pressure and temperature would have the same volume per pound as the mixture. Hence taking $m = 26.38$, the gas constant for the mixture is $\frac{1544}{26.38} = 58.53$, the volume of 1 lb. at atmospheric pressure and 32° F. is $\frac{358.7}{26.38} = 13.6$ cu. ft., and the difference $c_p - c_v = \frac{1.986}{26.38} = 0.0753$.

It is sometimes desirable to obtain the gas constant of a mixture from the weight composition. The application of Dalton's law leads to the result sought. Let $M_1, M_2, M_3, \ldots$ denote the weights of the several constituents as given by the weight composition, $B_1, B_2, B_3, \ldots$ the constants of these constituents, V the total volume, T the temperature of the mixture, $p_1, p_2, p_3, \ldots$ the partial pressures. Then assuming that each constituent obeys the law of perfect gases,

$$p_1 = M_1 B_1 \frac{T}{V}, \qquad p_2 = M_2 B_2 \frac{T}{V}, \qquad p_3 = M_3 B_3 \frac{T}{V}, \ldots$$

$$p = p_1 + p_2 + p_3 + \ldots = \frac{T}{V}(M_1 B_1 + M_2 B_2 + M_3 B_3 + \ldots) \quad (4)$$

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Let $$MB_m = M_1B_1 + M_2B_2 + M_3B_3 + \ldots \quad (5)$$
where $$M = M_1 + M_2 + M_3 + \ldots$$
is the weight of the mixture. From (4)

$$pV = MB_mT. \quad (6)$$

The constant B_m may therefore be regarded as the characteristic constant of the mixture. It is obtained from (5), which may be written in the more convenient form

$$B_m = \frac{\Sigma MB}{\Sigma M}. \quad (7)$$

Taking the weight composition of the producer gas in the preceding example the constant B_m is determined as follows

Constituent	M	B	MB
H_2	0.0068	765.87	5.208
CO	0.2547	55.14	14.084
CH_4	0.0121	96.31	1.165
CO_2	0.1001	35.09	3.513
N_2	0.6263	55.10	34.509
	1.0000		58.479

Since $\Sigma M = 1$, and $\Sigma MB = 58.479$, it follows that $B_m = 58.479$. It will be seen that this result is slightly different from the value 58.53 obtained from the volume composition. As a matter of fact, both values are in error due to the use of the approximate integral values of the molecular weights. Taking the exact values of m, the constant is found to be 58.50.

187. Specific Heat of Gases.—It is convenient in dealing with gases to refer specific heats to the mol rather than the pound as the unit of weight. Let γ denote the specific heat per mol, c the specific heat per pound; then

$$\gamma = mc; \qquad \gamma_v = mc_v; \qquad \gamma_p = mc_p.$$

Experiments on the specific heat of gases indicate that, in general, the specific heat increases as the temperature rises. The character of the variation of specific heat and temperature depends somewhat on the nature of the gas.

(*a*) *The Simple or Diatomic Gases.*—Experiments on the diatomic gases, H_2, O_2, N_2, and air justify two conclusions: (1)

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That the specific heat per mol is the same for all these gases. (2) That the variation of specific heat with temperature is expressed by a simple linear equation $\gamma = a + bT$. The following equations have been suggested.

By Langen $\gamma_p = 6.8 + 0.0012t.$
By Pier $\gamma_p = 6.9 + 0.0009t.$
By Holborn and Henning $\gamma_p = 6.58 + 0.001064t.$

In these formulas t denotes temperature on the C scale.

Pier's equation should probably be given the preference. Passing to the F scale and to absolute temperature the equation becomes

$$\gamma_p = 6.65 + 0.0005T. \qquad (1)$$

(*b*) *Carbon Dioxide.*—The most reliable experiments indicate that the specific heat of CO_2 cannot be expressed as a linear function of the temperature. Pier has proposed a third-degree equation to represent his experimental results. However, the following second-degree equation represents with fair accuracy the experiments up to a temperature of 4000° F.

$$\gamma_p = 7.22 + 3.7 \times 10^{-3}T - 0.528 \times 10^{-6}T^2. \qquad (2)$$

The expression for the specific heat per pound is

$$c_p = 0.164 + 0.084 \times 10^{-3}T - 0.012 \times 10^{-6}T^2. \qquad (2a)$$

In these formulas T denotes absolute temperature on the F scale.

(*c*) *Water Vapor.*—Near the saturation limit the specific heat of steam varies with the pressure as well as with the temperature. However, the water vapor in a gaseous mixture has a low pressure when the mixture has a low temperature, or if the mixture has a high pressure the temperature is correspondingly high. In either case the variation of specific heat with the pressure is negligible. The following equation represents very well the results of the Munich experiments at low temperatures and at the same time the experiments of Langen, Pier, and others at high temperatures.

$$\gamma_p = 7.12 + 1.44 \times 10^{-3}T + 0.125 \times 10^{-6}T^2. \qquad (3)$$

Since the difference between γ_p and γ_v is $AR = 1.986$, or 1.99 approximately, expressions for γ_v, the specific heat at con-

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stant volume are obtained by subtracting 1.99 from the first term of the expression for γ_p. Thus we have

for H_2, O_2, N_2, CO, and air

$$\gamma_v = 4.66 + 0.0005T; \tag{4}$$

for CO_2

$$\gamma_v = 5.23 + 3.7 \times 10^{-3}T - 0.528 \times 10^{-6}T^2; \tag{5}$$

for H_2O

$$\gamma_v = 5.13 + 1.44 \times 10^{-3}T + 0.125 \times 10^{-6}T^2. \tag{6}$$

Satisfactory experimental data on the specific heats of other important gases are lacking. For CH_4 and C_2H_4 the following formulas from Hütte may be accepted in the absence of anything better.

For CH_4

$$\gamma_p = 3.33 + 0.009T, \tag{7}$$

$$\gamma_v = 1.34 + 0.009T. \tag{8}$$

For C_2H_4

$$\gamma_p = 3.40 + 0.012T, \tag{9}$$

$$\gamma_v = 1.41 + 0.012T. \tag{10}$$

188. Specific Heat of a Gas Mixture.—Let $m_1, m_2, m_3, \ldots$ denote, respectively, the weights of the individual constituents in mols, and $\gamma_1, \gamma_2, \gamma_3, \ldots$ the corresponding specific heats. Then if γ denotes the specific heat of the mixture, we have

$$\gamma(m_1 + m_2 + m_3 + \ldots) = m_1\gamma_1 + m_2\gamma_2 + m_3\gamma_3 + \ldots$$

or

$$\gamma = \frac{\Sigma m\gamma}{\Sigma m}. \tag{1}$$

EXAMPLE. Find an expression for the specific heat at constant volume of the producer gas having the composition given in Art. 186.

The diatomic gases may be grouped together. Hence we have

	m	γ_v
H_2, N_2 and CO.....	0.92 mol	$4.66 + 0.0005T$
CH_4.....	0.02 mol	$1.34 + 0.009T$
CO_2.....	0.06 mol	$5.23 + 0.0037T - 0.528 \times 10^{-6}T^2$
	1.00	

$m\gamma_v$
$4.2872 + 0.00046T$
$0.0268 + 0.00018T$
$0.3138 + 0.000222T - 0.03168 \times 10^{-6}T^2$
$4.6278 + 0.000862T - 0.03168 \times 10^{-6}T^2$

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The expression for γ_v is therefore

$$\gamma_v = 4.6278 + 0.000862T - 0.03168 \times 10^{-6}T^2.$$

Since the weight of 1 mol is 26.38 lb., the expression for the specific heat per pound is

$$c_v = \frac{\gamma_v}{26.38} = 0.1754 + 0.0000326T - 0.001201 \times 10^{-6}T^2.$$

189. Adiabatic Changes of State.—The equations heretofore derived for adiabatic changes of state (See Art. 36) are not applicable when the specific heat of the gas is assumed to vary with the temperature. The modified relations for the case of variable specific heat are, however, readily obtained by a combination of fundamental equations.

The characteristic equation

$$pv = BT \tag{1}$$

and the energy equation

$$dq = du + Apdv \tag{2}$$

are valid, and the expression for the energy is, as before,

$$du = c_v dT. \tag{3}$$

The specific heat c_v is, however, given by the equation

$$c_v = a + bT + fT^2, \tag{4}$$

though the coefficient f may be taken as zero unless the gas has CO_2 and H_2O among its constituents. Combining (2), (3), and (4), the energy equation becomes

$$dq = (a + bT + fT^2)dT + Apdv, \tag{5}$$

and this becomes for an adiabatic change

$$0 = (a + bT + fT^2)dT + Apdv. \tag{6}$$

Eliminating the variable p between (1) and (6), and dividing the resulting relation by T, we have

$$\left(\frac{a}{T} + b + fT\right)dT + AB\frac{dv}{v} = 0. \tag{7}$$

Integrating between the limits 1 and 2, we obtain the following relation between the initial and final volumes and temperatures.

$$a \log_e \frac{T_2}{T_1} + b(T_2 - T_1) + \tfrac{1}{2}f(T_2^2 - T_1^2) = AB \log_e \frac{v_1}{v_2}. \tag{8}$$

The relation between pressures and temperatures is easily obtained by substituting for the ratio $\frac{v_1}{v_2}$ in (8). Thus from (1)

$$\frac{v_1}{v_2} = \frac{T_1}{T_2} \cdot \frac{p_2}{p_1},$$

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whence $$\log_e \frac{v_1}{v_2} = \log_e \frac{p_2}{p_1} + \log_e \frac{T_1}{T_2},$$

and (8) becomes

$$(a + AB) \log_e \frac{T_2}{T_1} + b(T_2 - T_1) + \tfrac{1}{2} f(T_2^2 - T_1^2) = AB \log_e \frac{p_2}{p_1}. \quad (9)$$

Equations (8) and (9) reduce to the simpler forms heretofore given when the specific heat is constant, that is, when $b = 0$, $f = 0$. Thus in (9), $a = c_v$, $a + AB = c_p$, $AB = c_p - c_v$, whence

$$c_p \log_e \frac{T_2}{T_1} = (c_p - c_v) \log_e \frac{p_2}{p_1}$$

or

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\frac{c_p - c_v}{c_p}} = \left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}}.$$

In the practical application of equations (8) and (9) the final temperature T_2 is usually the unknown quantity and the equations, being transcendental, must be solved by trial. Either equation can be thrown into the form

$$\log T_2 = L - MT_2 - NT_2^2 \quad (10)$$

Thus divide both members of (9) by 2.3026 $(a + AB)$. The division by 2.3026 reduces the Napierian logarithms to common logarithms, and the resulting equation is

$$\log \frac{T_2}{T_1} + \frac{b}{2.3026(a + AB)} (T_2 - T_1) + \frac{f}{2 \times 2.3026(a + AB)} (T_2^2 - T_1^2) = \frac{AB}{(a + AB)} \log \frac{p_2}{p_1}.$$

We have by transposition

$$\log T_2 = \log T_1 + \frac{AB}{a + AB} \log \frac{p_2}{p_1} + \frac{b}{2.3026(a + AB)} T_1 + \frac{f}{2 \times 2.3026(a + AB)} T_1^2 - \frac{b}{2.3026(a + AB)} T_2 - \frac{f}{2 \times 2.3026(a + AB)} T_2^2,$$

and since T_1, p_1 and p_2 are known quantities the sum of the first four terms of the second member is a known constant L. Having the equation in the form (10), values of the second member are

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calculated for values of T_2 near the probable final temperature and by a few trials a value of T_2 that satisfies the equation is obtained.

EXAMPLE. The specific heat of a gaseous mixture is given by the equation $c_v = 0.162 + 0.000026T$ and the constant AB is 0.072. The initial absolute temperature is $T_1 = 650$ and the gas is compressed from a volume of 10 cu. ft. to a volume of 2 cu. ft. Required the final temperature.

Inserting known values in (8), we have

$$0.162 \log_e \frac{T_2}{650} + 0.000026(T_2 - 650) = 0.072 \log_e \frac{10}{2}.$$

Dividing by 0.162×2.3026, this equation becomes

$$\log T_2 = \frac{0.072}{0.162} \log 5 + \log 650 + \frac{0.000026 \times 650}{0.162 \times 2.3026} - \frac{0.000026}{0.162 \times 2.3026} T_2$$

$$= 3.16887 - [\bar{5}.84324]\, T_2,$$

in which $[\bar{5}.84324]$ denotes the number whose logarithm is $\bar{5}.84324$. The simple adiabatic equation $\frac{T_2}{T_1} = \left(\frac{v_1}{v_2}\right)^{k-1}$ with $k = 1.4$ may be used to give an approximate value of T_2; thus

$$T_2 = 650\left(\frac{10}{2}\right)^{0.4} = 1237 \text{ approx.}$$

We choose therefore $T_2 = 1200$, 1250, and 1300, and arrange the computation as follows:

$T_2 =$	1200	1250	1300
$\log T_2 =$	3.07918	3.09691	3.11394
$\log M =$	$\bar{5}.84324$	$\bar{5}.84324$	$\bar{5}.84324$
$\log MT_2 =$	$\bar{2}.92242$	$\bar{2}.94015$	$\bar{2}.95718$
$MT_2 =$	0.08364	0.08712	0.09061
$L =$	3.16887	3.16887	3.16887
$L - MT_2 =$	3.08523	3.08175	3.07826

Inspection of these results shows that T_2 lies between 1200 and 1250 and nearer the former value. The simplest way of determining T_2 is to plot the two values 3.07918 and 3.09691 and connect the points with a straight line, then likewise plot the two values 3.08523, 3.08175 and connect these points with a straight line. The intersection shows that T_2 is 1214 very nearly.

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The external work performed in an adiabatic change of state is, as always, the decrease of intrinsic energy. Since $du = c_v dT$, the decrease of energy in thermal units per pound is

$$u_1 - u_2 = -\int_{T_1}^{T_2} c_v dT$$
$$= -\int_{T_1}^{T_2} (a + bT + fT^2) dT$$
$$= a(T_1 - T_2) + \tfrac{1}{2}b(T_1^2 - T_2^2) + \tfrac{1}{3}f(T_1^3 - T_2^3).$$

EXAMPLE. With the data given in the preceding example determine the work required to compress the gas. Take $p_1 = 14.7$ lb. per sq. in.

We have $a = 0.162$, $b = 0.000026$, $f = 0$, $T_1 = 650$, $T_2 = 1214$. Inserting these values in (11) the *increase* of energy is found to be 105.04 B. t. u. per pound of gas. Since $AB = 0.072$, $B = 55.99$, and from the initial conditions the weight M is

$$M = \frac{p_1 V_1}{BT_1} = \frac{144 \times 14.7 \times 10}{55.99 \times 650} = 0.5816 \text{ lb.}$$

Hence the work of compression is $777.64 \times 0.5816 \times 105.04 = 47410$ ft.-lb.

190. Combustion Reactions.—The term combustion is applied to the chemical combination of a fuel substance with oxygen. The fuels are usually composed of hydrogen and carbon, and the reaction is characterized by the evolution of heat. The product formed by the union of hydrogen and oxygen is water, H_2O, and that formed by the complete combination of carbon and oxygen is carbon dioxide, CO_2.

The principal facts relating to the combustion of a fuel are derived directly from the equation of the reaction. As an illustration of the method of writing such an equation, consider the combustion of alcohol, C_2H_6O. Since both C and H are present the products are CO_2 and H_2O. Hence write

$$C_2H_6O + \ldots . O_2 = \ldots . CO_2 + \ldots . H_2O,$$

leaving the blanks to be filled out. The number of atoms of C in the two members of the equation must be the same; hence 2 must be the coefficient preceding CO_2. Similarly, to get 6 atoms of H in each member, 3 must precede H_2O. In the second member there are consequently 7 atoms of O; hence the coefficient preceding O_2 must be 3. The reaction equation is therefore

$$C_2H_6O + 3O_2 = 2CO_2 + 3H_2O.$$

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The molecular weights involved are: C_2H_6O, 46; O_2, 32; CO_2, 44; H_2O, 18. Introducing these, we get the equation

$$46 + 3 \times 32 = 2 \times 44 + 3 \times 18$$

or $$46 + 96 = 88 + 54$$

Dividing by 46, the molecular weight of C_2H_6O,

$$1 + \frac{96}{46} = \frac{88}{46} + \frac{54}{46}$$

or $$1 + 2.087 = 1.913 + 1.174$$

Thus 1 lb. of alcohol requires for its combustion 2.087 lb. of oxygen and the products are 1.913 lb. of CO_2 and 1.174 lb. of H_2O.

Consider now the coefficient in the reaction equation. They are

$$1 \quad 3 = 2 \quad 3$$

From the equation of molecular weights we see that these coefficients are the number of mols involved. Thus the reaction equation may be written

1 mol C_2H_6O + 3 mols O_2 = 2 mols CO_2 + 3 mols H_2O.

Because of the invariable volume of 1 mol, the equation may also be interpreted as follows:

1 volume of C_2H_6O combines with 3 volumes of O_2 and forms 2 volumes of CO_2 and 3 volumes of H_2O.

The reaction is therefore accompanied by an increase of volume of 25 per cent.

The oxygen required for combustion is usually taken from the atmosphere. Atmospheric air is a mixture of about 21 per cent. of oxygen and 79 per cent. of nitrogen by volume; hence 1 mol of O_2 carries with it $\frac{79}{21} = 3.8$ mols N_2. If air instead of pure oxygen is used for the combustion of C_2H_6O, the equation for the process becomes:

1 mol C_2H_6O + 3 mols O_2 + 11.4 mols N_2 =
2 mols CO_2 + 3 mols H_2O + 11.4 mols N_2.

In this case there are initially 15.4 mols and after the combustion 16.4 mols; hence the increase of volume is $\frac{1}{15.4} = 0.065$.

In practice an excess of air over the amount required for the combustion is frequently used. This excess is usually 15 to

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25 per cent., though in alcohol motors an excess of 50 per cent. is recommended. Taking an excess of 0.50 for alcohol, the following schedules show the conditions before and after combustion

FUEL MIXTURE

			Mols		Lb.
Fuel		C_2H_6O =	1.0	1.0×46 =	46.0
Required		O_2 =	3.0	3.0×32 =	96.0
Neutral	Excess	O_2 =	1.5	1.5×32 =	48.0
	Nitrogen (1.5×11.4)	N_2 =	17.1	17.1×28 =	478.8
			22.6		668.8

PRODUCTS MIXTURE

	Mols		Lb.
CO_2	2	2×44 =	88
H_2O	3	3×18 =	54
O_2	1.5	1.5×32 =	48
N_2	17.1	17.1×28 =	478.8
	23.6		668.8

From these schedules the weight (or volume) of air used and the weight of the combustion products are readily obtained. For 46 lb. of alcohol 668.8 − 46 = 622.8 lb. of air is introduced; hence the air used per lb. of fuel is 622.8 ÷ 46 = 13.54 lb. The weights of CO_2 and H_2O formed are, respectively, 88 ÷ 46 = 1.91 lb. and 54 ÷ 46 = 1.17 lb. Taking 62° F. as the standard temperature and atmospheric pressure, the volume of one mol is 380.6 cu. ft. For 46 lb. of fuel 21.6 mols of air are used; hence the volume of air per pound of alcohol is $380.6 \times \frac{21.6}{46} = 178.7$ cu. ft. The apparent volume of the combustion products at 62° and atmospheric pressure, per pound of alcohol $380.6 \times \frac{23.6}{46} = 195.3$ cu. ft.

The partial pressures of the constituents of the products mixture are proportioned to the number of mols; thus if the total pressure of the mixture is 14.7 lb., the partial pressures are

CO_2, $\frac{2}{23.6} \times 14.7 = 1.24$ lb. $\quad O_2$, $\frac{1.5}{23.6} \times 14.7 = 0.93$ lb.

H_2O, $\frac{3}{23.6} \times 14.7 = 1.87$ lb. $\quad N_2$, $\frac{17.1}{23.6} \times 14.7 = 10.65$ lb.

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Reference to the steam table shows that at a pressure of 1.87 lb. per sq. in. saturated steam has a temperature of 124° F.; if, therefore, the temperature of the mixture is higher than 124°, the H_2O constituent is in the form of superheated vapor and at this low pressure it may be considered a perfect gas. The partial pressures are in this case those calculated. Suppose, however, that the mixture is cooled to the standard temperature 62° F. Part of the H_2O constituent must condense and the pressure of the mixture of water and steam at 62° F. is 0.275 lb. per sq. in., leaving $14.7 - 0.275 = 14.425$ lb. as the sum of the pressures of the other constituents. The partial pressures are again proportional to the weights in mols, thus:

CO_2 2.0 mols	Pressure of $CO_2 = \frac{2}{20.6} \times 14.425 =$	1.40 lb.
O_2 1.5 mols	Pressure of $O_2 = \frac{1.5}{20.6} \times 14.425 =$	1.05 lb.
N_2 17.1 mols	Pressure of $N_2 = \frac{17.1}{20.6} \times 14.425 =$	11.97 lb.
20.6 mols		

For a temperature of 62° and atmospheric pressure the volume of the products of combustion, was found to be 195.3 cu. ft., on the assumption that the H_2O remained in the gaseous state. The actual volume, taking account of the condensation of steam, is found by comparing the apparent and actual partial pressures of one of the other constituents, as nitrogen. If the nitrogen occupies the volume 195.3 cu. ft. at a partial pressure of 10.65 lb., then at a pressure of 11.97 lb. and at the same temperature, it will occupy the volume $195.3 \times \frac{10.65}{11.97} = 173.8$ cu. ft. This is the actual volume of the products of combustion per pound of alcohol.

191. Combustion of a Fuel Gas.—The gaseous fuels, as producer gas, blast-furnace gas, natural gas, etc. are mixtures of various fuel constituents along with non-combustible constituents. In calculating the air required and the products of combustion, it is necessary to write the reaction for each of the fuel constituents, multiply the coefficients in each by the weight of the constituent, and combine the results. The following example illustrates the procedure.

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EXAMPLE. Determine the air used and the products of combustion formed when the producer gas whose composition was given in Art. 186 is burned with 20 per cent. excess of air.

Volume composition Mols	Reaction equations	Coefficients
$H_2 = 0.09$	$H_2 + \frac{1}{2}O_2 = H_2O$	$1 \quad \frac{1}{2} = 1$
$CO = 0.24$	$CO + \frac{1}{2}O_2 = CO_2$	$1 \quad \frac{1}{2} = 1$
$CH_4 = 0.02$	$CH_4 + 2O_2 = CO_2 + 2H_2O$	$1 \quad 2 = 1 \quad 2$
$CO_2 = 0.06$		
$N_2 = 0.59$		

Multiplying the coefficient of O_2, CO_2, and H_2O, respectively by the weights of the respective constituents in mols, the following is obtained

Constituent	Required O_2	CO_2	H_2O
H_2.....	$0.09 \times \frac{1}{2} = 0.045$	.....	$0.09 \times 1 = 0.09$
CO.....	$0.24 \times \frac{1}{2} = 0.12$	$0.24 \times 1 = 0.24$	.....
CH_4.....	$0.02 \times 2 = 0.04$	$0.02 \times 1 = 0.02$	$0.02 \times 2 = 0.04$
	0.205	0.26	0.13
20 per cent. excess.....	0.041		
	0.246		

Nitrogen introduced with air, $0.246 \times 3.8 = 0.935$ mol. Air required $= 0.246 + 0.935 = 1.181$ mols. Hence 1.181 cu. ft. of air is the volume required for the combustion of one cubic foot of the producer gas.

The compositions of the mixture of producer gas and air and of the mixture of products are given by the following schedules.

Original Mixture	Mols
H_2.....	0.09
CO.....	0.24
CH_4.....	0.02
CO_2.....	0.06
O_2.....	0.246
N_2....0.935 + 0.59 =	1.525
	2.181

Mixture of Products	Mols
CO_2.....0.26 + 0.06 =	0.32
H_2O.....	0.13
Excess O_2.....	0.041
N_2.....	1.525
	2.016

The contraction of volume is $2.181 - 2.016 = 0.165$ mol, or about 7.6 per cent. Taking the pressure of the products mixture as 14.7 per sq. in., the partial pressure of the H_2O constituent is $\frac{0.13}{2.016} \times 14.7 = 0.948$ lb. per sq. in. The saturation temperature of steam corresponding to this pressure is 100° F., and it is important to note that no condensation of water vapor can occur until the temperature of the mixture is reduced below this point.

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192. Fundamental Equations of the Combustion Process.— During the process of combustion the constitution of the gaseous mixture is continually changing. The fuel constituents, as H_2 and CO, are disappearing and the products CO_2 and H_2O are being formed; only the neutral constituent remains unchanged. We introduce a variable z to denote the progress of the chemical reaction; thus when the combustion starts $z = 0$, when one-half of the fuel constituent has been burned $z = 0.5$, and at the end of the combustion $z = 1$. The following notation is used for the weights (in pounds) of the constituents.

Original Mixture		Mixture of Products	
M'	= weight of combustible gas,	M_1	= weight of CO_2 formed,
M''	= weight of O_2 required to burn M',	M_2	= weight of H_2O formed,
M'''	= weight of neutral gas present.	M'''	= weight of neutral.

The total weight of the mixture is denoted by M; hence

$$M = M' + M'' + M''' = M_1 + M_2 + M'''. \qquad (1)$$

When the fraction z of the fuel has been burned the constitution of the mixture is as follows:

$M'(1 - z)$ = weight of fuel constituent remaining,
$M''(1 - z)$ = weight of required O_2 remaining,
M''' = weight of neutral gas,
$M_1 z$ = weight of CO_2 formed,
$M_2 z$ = weight of H_2O formed.

We have now to deduce expressions for the properties of this mixture, in particular the gas constant B and the intrinsic energy U. The constituents all occupy the total volume V of the mixture and have the same temperature T; hence, denoting the partial pressures by p', p'', etc., the following equations are obtained.

$$\begin{aligned} p'V &= M'(1 - z)B'T, \\ p''V &= M''(1 - z)B''T, \\ p'''V &= M'''B'''T, \\ p_1V &= M_1 z B_1 T, \\ p_2V &= M_2 z B_2 T. \end{aligned}$$

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By Dalton's law the pressure p of the mixture is the sum of the partial pressures; hence adding the preceding equations, the resulting equation is

$$pV = T\,[M'B' + M''B'' + M'''B''' - z\,(M'B' + M''B'' - M_1B_1 - M_2B_2)]. \quad (2)$$

We shall denote by the subscript m properties of the original mixture of fuel gas and air and by the subscript p the properties of the mixture of products. Therefore let

$$\frac{M'B' + M''B'' + M'''B'''}{M} = B_m,$$

$$\frac{M_1B_1 + M_2B_2 + M'''B'''}{M} = B_p.$$

Then $$\frac{M'B' + M''B'' - M_1B_1 - M_2B_2}{M} = B_m - B_p,$$

and (2) becomes

$$pV = MT[B_m - z(B_m - B_p)], \quad (3)$$

or $$pv = T[B_m - z(B_m - B_p)].$$

For $z = 0$, (3) becomes

$$pv_m = B_mT, \quad (4)$$

and for $z = 1$,

$$pv_p = B_pT. \quad (5)$$

It appears, therefore, that B_m is the gas constant of the original mixture, B_p is the constant of the products mixture, and that $B_m - z(B_m - B_p)$ is the constant for the intermediate state indicated by the variable z.

The intrinsic energy of unit weight of a gas is given by the expression

$$u = \int_0^T c_v dT + u_0, \qquad \text{(See Art. 34)}$$

and for all the gaseous constituents of the mixture except CO_2 and H_2O, the specific heat c_v is a linear function of the temperature. Thus for the fuel constituent

$$c_v' = a' + b'T,$$

for the oxygen $$c_v'' = a'' + b''T,$$

for the neutral $$c_v''' = a''' + b'''T + f'''T^2.$$

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Introducing these expressions in the equation for u, we have

$$u' = a'T + \tfrac{1}{2}b'T^2 + u_0'$$
$$u'' = a''T + \tfrac{1}{2}b''T^2 + u_0'', \text{ etc.}$$

The specific heat of CO_2 is given by a second degree function, thus

$$c_{v_1} = a_1 + b_1T + f_1T^2,$$

whence $$u_1 = a_1T + \tfrac{1}{2}b_1T^2 + \tfrac{1}{3}f_1T^3 + u_{0_1}.$$

Similarly, for the water vapor, the expressions for the energy is

$$u_2 = a_2T + \tfrac{1}{2}b_2T^2 + \tfrac{1}{3}f_2T^3 + u_{0_2}.$$

The energy of the mixture in the state indicated by z is the sum of the energies of the constituents, and these are as follows:

Fuel	$M'(1-z)\ (a'T + \tfrac{1}{2}b'T^2 + u_0')$,
Oxygen	$M''(1-z)\ (a''T + \tfrac{1}{2}b''T^2 + u_0'')$,
Neutral	$M'''(a'''T + \tfrac{1}{2}b'''T^2 + \tfrac{1}{3}f'''T^3 + u_0''')$,
CO_2	$M_1z(a_1T + \tfrac{1}{2}b_1T^2 + \tfrac{1}{3}f_1T^3 + u_{0_1})$,
H_2O	$M_2z(a_2T + \tfrac{1}{2}b_2T^2 + \tfrac{1}{3}f_2T^3 + u_{0_2})$.

Adding these expressions we obtain for the energy of M lb. of the mixture

$$\begin{aligned} U = {} & M'u_0' + M''u''_0 + M'''u'''_0 \\ & -z[M'u'_0 + M''u''_0 - M_1u_{0_1} - M_2u_{0_2}] \\ & +T[M'a' + M''a'' + M'''a'''] \\ & -zT[M'a' + M''a'' - M_1a_1 - M_2a_2] \\ & +\tfrac{1}{2}T^2[M'b' + M''b'' + M'''b'''] \\ & -\tfrac{1}{2}zT^2[M'b' + M''b'' - M_1b_1 - M_2b_2] \\ & +\tfrac{1}{3}T^3[M'''f''' + z(M_1f_1 + M_2f_2)]. \end{aligned} \qquad (7)$$

Dividing the second member of this equation by M, the weight of the mixture, the result is the energy per unit weight.

We consider now the interpretation of the separate terms, assuming that each has been divided by M. Let the subscript m indicate the original mixture $M' + M'' + M'''$, and the subscript p the products mixture $M_1 + M_2 + M'''$. Then the specific heats of the two mixtures are respectively

$$c_{v_m} = a_m + b_mT + f_mT^2$$
$$c_{v_p} = a_p + b_pT + f_pT^2,$$

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in which the constants a_m, b_m, a_p, b_p are given by the following.

$$\left.\begin{aligned} a_m &= \frac{M'a' + M''a'' + M'''a'''}{M}, \\ a_p &= \frac{M_1a_1 + M_2a_2 + M'''a'''}{M}, \\ b_m &= \frac{M'b' + M''b'' + M'''b'''}{M}, \\ b_p &= \frac{M_1b_1 + M_2b_2 + M'''b'''}{M}. \end{aligned}\right\} \tag{8}$$

Subtracting the preceding expressions, we obtain

$$\left.\begin{aligned} a_m - a_p &= \frac{M'a' + M''a'' - M_1a_1 - M_2a_2}{M}, \\ b_m - b_p &= \frac{M'b' + M''b'' - M_1b_1 - M_2b_2}{M}. \end{aligned}\right\} \tag{9}$$

In the original mixture CO_2 is usually the only constituent with a second degree term in the expression for c_v and this is contained in the neutral. Hence we have

$$f_m = \frac{M'''f'''}{M}, \qquad f_p = \frac{M'''f''' + M_1f_1 + M_2f_2}{M}, \tag{10}$$

and

$$f_m - f_p = -\frac{M_1f_1 + M_2f_2}{M}. \tag{11}$$

In most cases f''' is zero or so small that it is negligible.

We may also write

$$\left.\begin{aligned} u_{0m} &= \frac{M'u_0' + M''u_0'' + M'''u_0'''}{M}, \\ u_{0p} &= \frac{M_1u_{01} + M_2u_{02} + M'''u_0'''}{M}, \end{aligned}\right\} \tag{12}$$

whence

$$u_{0m} - u_{0p} = \frac{M'u_0' + M''u_0'' - M_1u_{01} - M_2u_{02}}{M}. \tag{13}$$

Substituting in (7) the constants defined by the equations (8) to (13), we have for the energy per unit weight of the mixture the expression

$$\frac{U}{M} = u = u_{0m} - z(u_{0m} - u_{0p}) + T[a_m - z(a_m - a_p)] + \tfrac{1}{2}T^2[b_m - z(b_m - b_p)] + \tfrac{1}{3}T^3[f_m - z(f_m - f_p)]. \tag{14}$$

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Taking $z = 0$, we get for the energy of the original mixture per unit weight

$$u_m = u_{0m} + a_m T + \tfrac{1}{2} b_m T^2 + \tfrac{1}{3} f_m T^3, \tag{15}$$

and with $z = 1$, we have for the energy of the mixture of products

$$u_p = u_{0p} + a_p T + \tfrac{1}{2} b_p T^2 + \tfrac{1}{3} f_p T^3. \tag{16}$$

For the original mixture we have

$$pv_m = B_m T$$

or $$Apv_m = AB_m T,$$

and since $$i = u + Apv,$$

the thermal potential of the original mixture is

$$i_m = u_{0m} + (a_m + AB_m) T + \tfrac{1}{2} b_m T^2 + \tfrac{1}{3} f_m T^3. \tag{17}$$

Likewise, for the products mixture

$$i_p = u_{0p} + (a_p + AB_p) T + \tfrac{1}{2} b_p T^2 + \tfrac{1}{3} f_p T^3. \tag{18}$$

The product AB_m is the difference between the specific heats at constant volume and constant pressure of one pound of the original mixture; that is, if

$$c_{vm} = a_m + b_m T$$

and $$c_{pm} = a'_m + b_m T,$$

then $$AB_m = c_{pm} - c_{vm} = a'_m - a_m,$$

whence $$a_m + AB_m = a'_m.$$

Likewise $$a_p + AB_p = a'_p.$$

Equations (17) and (18) may therefore be written

$$i_m = u_{0m} + a'_m T + \tfrac{1}{2} b_m T^2 + \tfrac{1}{3} f_m T^3, \tag{19}$$

$$i_p = u_{0m} + a'_p T + \tfrac{1}{2} b_p T^2 + \tfrac{1}{3} f_p T^2. \tag{20}$$

193. Heat of Combustion.—The union of any combustible material with oxygen is accompanied by the evolution of heat; and the heat thus generated when a unit weight of a fuel is burned is called the **heating value** of the fuel.

In the experimental determination of the heat of combustion, the heat generated during the process is absorbed usually by cold water. Hence, applying the energy equation to the combustion process, we have for the heat rejected

$$-{}_1Q_2 = U_1 - U_2 - \int_{V_1}^{V_2} p dV, \tag{1}$$

and $-{}_1Q_2$ divided by the weight of fuel present gives the heating

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value. In order to make the definition of heating value precise, the conditions under which the combustion proceeds must be specified. In the first place, the final temperature of the products of combustion must be the same as the temperature of the original fuel mixture. Secondly, in the case of gaseous fuels, it is specified that either the volume or the pressure shall be kept constant during the process. If the volume remains constant the external work is zero, and

$$-{}_1Q_2 = U_1 - U_2, \tag{2}$$

that is, the heat rejected is the difference between the intrinsic energy of the original mixture and the energy of the products mixture. If the pressure is kept constant, we have

$$-{}_1Q_2 = I_1 - I_2. \tag{3}$$

Equations (15)–(18) of the preceding article give expressions for u and i, but these apply to unit weight of the total mixture rather than to unit weight of the fuel. Since in M lb. of the mixture the weight of the fuel constituent is M' lb., the values of u and i per pound of combustible are obtained by multiplying these expressions by $\frac{M}{M'}$. Therefore, denoting by H_v the heat rejected per pound of fuel when the process is at constant volume, we have

$$H_v = \frac{M}{M'}(u_m - u_p); \tag{4}$$

and likewise denoting by H_p the heat rejected at constant pressure,

$$H_p = \frac{M}{M'}(i_m - i_p). \tag{5}$$

The difference $u_{0m} - u_{0p}$ of the energy constants may be denoted $\frac{M'}{M}H_0$. Substituting the expressions for u_m, u_p, i_m, i_p in (4) and (5) with the condition that the temperature of the products is the same as the temperature of the fuel mixture, we obtain

$$H_v = H_0 + \frac{M}{M'}[(a_m - a_p)T + \tfrac{1}{2}(b_m - b_p)T^2 + \tfrac{1}{3}(f_m - f_p)T^3], \tag{6}$$

$$H_p = H_0 + \frac{M}{M'}[(a'_m - a'_p)T + \tfrac{1}{2}(b_m - b_p)T^2 + \tfrac{1}{3}(f_m - f_p)T^3]. \tag{7}$$

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It appears, therefore, that the heat of combustion, H_v or H_p, is made up of two parts: one, a constant H_0, which may be regarded as the heat of combustion for $T = 0$; the other, a term depending on the temperature and the specific heats of the original and final gas mixtures. The dependence of H_v or H_p on the specific heats is shown more clearly by writing (6) and (7) in the equivalent forms

$$H_p = H_0 + \frac{M}{M'}\int_0^T (c_{vm} - c_{vp})dT, \tag{8}$$

$$H_v = H_0 + \frac{M}{M'}\int_0^T (c_{pm} - c_{pp})dT. \tag{9}$$

If the specific heat c_{vp} of the products mixture and c_{vm} of the original mixture are equal, the second term reduces to zero and $H_v = H_0$ at all temperatures. In any case, H_0 is the important term and the variation of H_v (or H_p) with the temperature is not large.

The difference between H_p and H_v is found by subtracting (6) from (7); thus

$$H_p - H_v = \frac{M}{M'}[(a'_m - a_m) - (a'_p - a_p)]T$$

$$= \frac{M}{M'}(AB_m - AB_p)T = \frac{A}{M'}p(V_m - V_p). \tag{10}$$

If the reaction produces a contraction of molecular volume, that is, if $V_m > V_p$, then H_p exceeds H_v, and vice versa. It there is no change of molecular volume the two heating values are identical.

194. Higher and Lower Heating Values.—In the preceding derivation of the expression for H_v and H_p it has been assumed that all the gaseous constituents remained in the gaseous form throughout the combustion process. However, in the experimental determination of heating values, as with the Junkers calorimeter, the temperature of the products is sufficiently low to cause condensation of a part of the H_2O constituent. The latent heat of the condensed water is thus added to the H_p given by (7) and the result is an experimental value H'_p higher than H_p. These two values are called, respectively, the *higher* and the *lower* heating values. For a fuel containing no hydrogen, there is, of course, no steam to condense, and therefore the fuel has only the one heating value.

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The difference between H_p and H'_p depends upon the conditions prevailing during the experiment; it varies with the temperature adopted, with the pressure, and with the weight of air used.

Let T_1 denote the absolute temperature for which H_p is to be determined, that is, the temperature of the original mixture and the temperature to which the products are cooled; and let T_2 denote the absolute temperature at which condensation begins. The temperature T_2 can always be determined, since it is the saturation temperature corresponding to the partial pressure of the water vapor in the mixture of products.

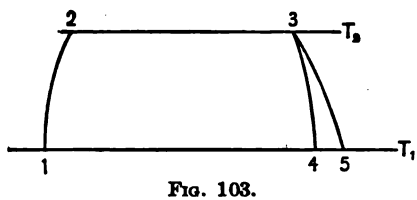


FIG. 103.

We may conceive the combustion at temperature T_1 replaced by a series of processes which produces the same thermal effect. Referring to Fig. 103, let point 1 represent the state of the gas mixture at temperature T_1 before combustion, and point 4 the state of the products mixture after combustion. Then the heating value is given by the equation

$$H_p = \frac{M}{M'}(i_1 - i_4). \tag{1}$$

Assume now that the gas mixture is heated from T_1 to T_2, as indicated by the path 1–2; that combustion then ensues at temperature T_2, the point 3 representing the products mixture at temperature T_2; and, finally, that the products are cooled from T_2 to T_1, as indicated by the path 3–4. The heat given up in the three processes per pound of mixture is

$$q = (i_1 - i_2) + (i_2 - i_3) + (i_3 - i_4) = i_1 - i_4, \tag{2}$$

and per pound of fuel it is

$$\frac{M}{M'}q = \frac{M}{M'}(i_1 - i_4) = H_p. \tag{3}$$

In the cooling process represented by 3–4 it is assumed that the water vapor in the products mixture remains in the gaseous state. When part of the water vapor condenses, the products mixture after cooling to T_1 is in a different state which may be represented

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by point 5 The total heat given up when the path 3–5 is followed is

$$q' = (i_1 - i_2) + (i_2 - i_3) + (i_3 - i_5) = (i_1 - i_5) \quad (4)$$

and we get for the higher heating value

$$H'_p = \frac{M}{M'} q' = \frac{M}{M'} (i_1 - i_5). \quad (5)$$

From (2) and (4) we obtain

$$q' - q = (i_3 - i_5) - (i_3 - i_4). \quad (6)$$

Consider now the constituents of the products mixture aside from H_2O. For the final states 4 and 5 the thermal potential of these constituents is the same. When there is condensation of water vapor the volume of the mixture decreases, and at the same time the partial pressure of the constituents other than H_2O is raised so that the product pV of those constituents remains unchanged (Art. 190); consequently the sum $u + pv$, or i, remains unchanged. It follows that the difference $q' - q$ in (6) is given by the difference $(i_3 - i_5) - (i_3 - i_4)$ for the water vapor alone. The term $i_3 - i_4$ is readily calculated on the assumption that the water vapor remains in the gaseous state and is cooled at constant pressure. Thus

$$i_3 - i_4 = \int_{T_1}^{T_2} c_p dT = \int_{T_1}^{T_2} (a_2 + b_2 T + f_2 T^2) dT. \quad (7)$$

It is sufficiently exact for the cases that arise in practice to take 0.443 as the mean specific heat of water vapor for the temperature range involved. Then

$$i_3 - i_4 = 0.443(t_2 - t_1). \quad (8)$$

To determine the difference $i_3 - i_5$, we observe that i_3 is the saturation value of i for the temperature T_2, and that for the state 5 in which the vapor is partly condensed, $i_5 = i_1 + xr_1$. The quality x is easily determined from a consideration of the volume occupied by the mixture.

Having the values i_3, i_5, and $(i_3 - i_4)$ for 1 lb. of water vapor, the difference between the two heating values is

$$H'_p - H_p = \frac{M_2}{M'} [(i_3 - i_5) - (i_3 - i_4)], \quad (9)$$

in which M_2 denotes, as usual, the weight of water vapor in the mixture of products.

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EXAMPLE. Calculate the difference between the higher and lower heating values of hydrogen at a pressure of 14.7 lb. per sq. in. and 62° F. Assume that the theoretical amount of air is used.

The mixture of constituents and products are given in the following schedules.

	Original mixture			Mixture of products	
	Mols	Lb.		Mols	Lb.
H_2.....	1.0	2.0	H_2O.....	1.0	18.2
O_2.....	0.5	16.0	N_2.....	1.9	53.2
N_2.....	1.9	53.2		—	—
	—	—		2.9	71.2
	3.4	71.2			

The partial pressures in the products mixture are:

of H_2O $\quad 14.7 \times \frac{1}{2.9} = 5.07$ lb. per sq. in.

of N_2 $\quad 14.7 \times \frac{1.9}{2.9} = 9.63$ lb. per sq. in.

From the steam table the saturation temperature corresponding to the pressure 5.07 lb. is 163° F.; this, therefore, is the temperature t_3 at which condensation begins.

Consider now the conditions represented by points 4 and 5, Fig. 103. If the water vapor were in the gaseous condition the volume of 2.9 mols of mixture at 62° F. would be

$$2.9 \times 358.7 \times \frac{522}{492} = 1103.6 \text{ cu. ft.}$$

If, however, the H_2O constituent is a mixture of water and saturated vapor at 62° F., the pressure of the vapor is 0.275 lb. (see the steam tables) and consequently the pressure of the nitrogen is $14.7 - 0.275 = 14.425$ lb. The increase in the pressure of the N_2 from 9.63 to 14.425 lb. at the same temperature, 62° F., requires a reduction in volume, and the volume corresponding to the condition 5 is

$$1103.6 \times \frac{9.63}{14.425} = 736.8 \text{ cu. ft.}$$

This volume contains 18 lb. water and water vapor at 62°, at which temperature the specific volume of steam is 1128 cu. ft. Hence the quality of the vapor is

$$x = \frac{736.8}{18 \times 1128} = 0.0363.$$

The thermal potential of the vapor in the state 5 is accordingly

$$i_5 = i_1' + xr_1 = 30 + 0.0363 \times 1057.1 = 68.4 \text{ B. t. u.}$$

The thermal potential of saturated steam at 163° F. is 1132.1 B. t. u.; hence

$$i_3 - i_5 = 1132.1 - 68.4 = 1063.7 \text{ B. t. u.}$$

For the decrease of thermal potential $i_3 - i_4$ we have from (8)

$$i_3 - i_4 = 0.443\ (163 - 62) = 44.8 \text{ B. t. u.}$$

Hence

$$(i_3 - i_5) - (i_3 - i_4) = 1063.7 - 44.8 = 1018.9 \text{ B. t. u.}$$

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Since $\frac{M_2}{M'} = \frac{18}{2} = 9$. the difference between the heating values is $9 \times 1018.9 = 9170$ B. t. u.

The higher heating value of hydrogen is usually given as 62,100 B. t. u. per pound; hence the lower heating value is 52,930 B. t. u.

In estimating the efficiency of any process that involves combustion, the heating value of the fuel is taken as the energy supplied and this is compared with the energy obtained in the process. Thus in the case of the internal combustion engine the efficiency of the motor is the ratio of the work delivered to the heating value of the fuel used. Which of the two heating values, the higher or the lower, should be charged against the engine? Before answering this question let us consider the conditions of operation in the internal combustion engine. As shown in the example of Art. 190, the partial pressure of the H_2O constituent in the mixture of products is a small part of the total pressure; this is always the case with the fuels ordinarily used. As a result, when the exhaust gas has its pressure reduced to nearly atmospheric pressure the pressure of the water vapor is only about 1 to 2 lb. per sq. in. and the corresponding saturation temperature is 100 to 125° F. Experience shows, however, that the original fuel mixture, even before compression, has a higher temperature than this; so that condensation of water vapor is out of the question. It is clear, therefore, that the lower heating value should always be used in estimating efficiencies.

195. Heating Values per Unit Volume.—Since a fuel gas is usually measured by volume rather than by weight, it is convenient to express heating values in terms of volumes. For this purpose a standard pressure and temperature, as 14.7 lb. per sq. in. and 62° F., must be assumed. The volume of 1 mol under these conditions is 380.6 cu. ft. and the volume of 1 pound is $380.6/m$, where m denotes the molecular weight of the constituent; hence if H is the heating value per pound, the heating value per cubic foot is

$$H \frac{m}{380.6} \text{ B. t. u.}$$

For example, H for CO is 4390 B. t. u. per lb., and $m = 28$. For one cubic foot at 14.7 lb. and 62° F. the heating value is therefore

$$4380 \times \frac{28}{380.6} = 322 \text{ B. t. u.}$$

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If the gas has some other pressure and temperature, as p_1 and t_1, multiply the heating value per cu. ft. under the standard conditions by $\frac{35.5p_1}{t_1+459.6}$. $\left(35.5 = \frac{521.6}{14.7}\right)$

For example, fuel gas in a gas engine cylinder has a pressure of 13.8 lb. per sq. in. and a temperature of 190° F. Under these conditions the heating value of 1 cu. ft. of the CO constituent is

$$322 \times \frac{35.5 \times 13.8}{190 + 459.6} = 243 \text{ B. t. u.}$$

The following table gives the heating values of some of the common constituents of fuel gases. The lower heating value is deduced from the higher on the assumption that the theoretical weight of air is used and that the standard temperature is 62° F.

Gas		Heating value per pound		Heating value per cu. ft. at 14.7 lb. and 62° F.
		High	Low	Low
Carbon monoxide	CO	.....	4,380	322
Hydrogen	H_2	62,100	52,930	280
Methane	CH_4	23,850	21,670	913
Ethane	C_2H_6	22,230	20,500	1,618
Ethylene	C_2H_4	21,600	20,420	1,504
Acetylene	C_2H_2	24,600	21,020	1,437

The heating value per unit volume of a mixture of several fuel constituents is readily obtained. The following example illustrates the method.

EXAMPLE. Find the heating value per cubic foot under standard conditions of the producer gas mentioned in Art. 186.

Constituent	Volume v	Heating value H	vH
H_2	0.09	280	25.2
CO	0.24	322	77.28
CH_4	0.02	913	18.26
CO_2	0.06	0	0
N_2	0.59	0	0
	1.00		120.7

Thus the lower heating value per cu. ft. is 120.7 B. t. u.

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The same method may be used to find the lower heating value per pound when the weight composition is given. The method, however, does not apply in the case of the higher heating value.

EXERCISES

The following table gives the approximate composition by volume of certain fuel gases.

	H_2	CO	CH_4	C_2H_4	O_2	CO_2	N_2
1. Blast furnace gas.....	0.04	0.27	....	....	....	0.10	0.59
2. Producer gas.....	0.15	0.22	0.03	....	....	0.09	0.51
3. Water gas.....	0.50	0.45	....	....	....	0.03	0.02
4. Carbureted water gas..	0.30	0.27	0.25	0.15	....	0.01	0.02
5. Natural gas.....	0.02	0.07	0.93	....	0.005	0.005	0.03

1. Find the composition by weight of each of these gases.

2. For each of the gases find the volume of air required for the combustion of 1 cu. ft. of the gas.

Ans. { 2. 1.176 cu. ft.
5. 8.98 cu. ft.

3. Using 15 per cent. excess air, make up schedules of the mixture of fuel and air and of the mixture of products. Show the composition of each mixture in mols and in pounds.

4. From these schedules calculate the constants B_m of the original mixtures and the constants B_p of the mixtures of the products.

Ans. { 1. $B_m = 53.82$, $B_p = 49.33$
3. $B_m = 61.40$, $B_p = 53.35$
4. $B_m = 56.42$, $B_p = 54.36$

5. Derive expressions for the specific heats c_p and c_v per pound for all the mixtures.

6. Find the lower heating value of each gas per cubic foot under standard conditions.

Ans. { 1. 98 B. t. u.
2. 140 B. t. u.
3. 285 B. t. u.
4. 625 B. t. u.
5. 858 B. t. u.

7. Find the contraction in volume of each gas when burned with 15 per cent excess air.

8. From the composition of the mixture of products determine in each case the partial pressure of the H_2O constituent, assuming that the pressure of the mixture is 14.7 lb. per sq. in. Determine the temperature at which condensation of H_2O begins.

9. From the general expression for the heat of combustion H_p show that H_p has a maximum or minimum value at some temperature. Derive an expression from which the temperature at which the maximum or minimum occurs may be calculated.

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10. The lower heating value of CH_4 at constant pressure is given as 21,670 B. t. u. per pound. If this value is associated with the temperature 62° F., what is the heating value at 170° F.? At 500° F.?

Ans. (*a*) 21,666 B. t. u.; (*b*) 21,658 B. t. u.

11. Find the difference between H_p and H_v (*a*) for hydrogen; (*b*) for CO; (*c*) for CH_4. Ans. (*a*) 259 B. t. u.; (*b*) 18.5 B. t. u.; (*c*) 0

12. Calculate the difference between the higher and lower heating values of CH_4. Assume that the standard temperature is 62° F., that the pressure is 14.7 lb., and that the theoretical amount of air is used. Ans. 2185 B. t. u.

13. Calculate the difference $H'_p - H_p$ for CH_4, assuming a temperature of combustion of 100°. Use theoretical amount of air. Ans. 1677 B. t. u.

14. Find the difference between H'_p and H_p for alcohol C_2H_6O, taking the temperature of combustion at 62° and using theoretical weight of air.

Ans. 1110 B. t. u.

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CHAPTER XVI

INTERNAL COMBUSTION ENGINES

196. Comparison of Steam and Air.—Water vapor as a heat medium has one important disadvantage. The rigid relation between the temperature and pressure of saturated steam renders impossible the use of high temperatures. At a pressure of 250 lb. per sq. in. the saturation temperature is about 400° F., and if the boiler pressure were raised to 1000 lb. the temperature would be raised to only 545° F. As has been shown, high efficiency of a heat motor is dependent upon a large temperature difference between the entering medium and the refrigerator. With steam as a medium the temperature difference is limited by the permissible boiler pressure, and the steam engine is necessarily a motor of low efficiency. The temperature range may be increased by superheating the steam but, as shown heretofore, the cycle efficiency is but slightly increased.

With air as a medium, it is possible to raise the temperature nearly to the temperature of the furnace and still keep the pressure within any desired limits. A large temperature range with a corresponding high efficiency may presumably be attained.

As regards possible efficiency, air has a decided advantage over steam; in another respect, however, steam has an advantage over air. Because of the high latent heat of steam, a given volume of steam can deliver to the working cylinder a much larger quantity of heat than an equal volume of air; consequently, for the same power, the air engine must have greater bulk than the steam engine.

197. Hot-air Engines.—Heat motors that employ air or some other permanent gas as a working fluid may be divided into two chief classes: (1) Motors in which the furnace is exterior to the working cylinder, so that the medium is heated by conduction through metal walls. (2) Motors in which the medium is heated directly in the working cylinder by the combustion of some gaseous or liquid fuel. Air motors of the first class are

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usually designated as *hot-air engines*. The principal engines of this class are the Stirling engine designed by Robert Stirling in 1816, and the Ericsson engine. The engines for the 2200-ton vessel *Ericsson* had four single-acting working cylinders each 14 ft. in diameter with 6 ft. stroke. At a speed of 9 rev. per min. the engines developed 300 horsepower.

While the hot-air engine with exterior furnace should apparently be an efficient heat motor, experience has proved the contrary. The difficulty lies in the slow rate of absorption of heat by any gas. Even with high furnace temperatures and comparatively large heating surfaces, it has been found impossible to get a high temperature in the working medium. Furthermore, if the air could be effectively heated, the metal surfaces separating the furnace from the hot medium would be destroyed; hence, while high temperature of air is necessary for high efficiency, low temperature is necessary to secure the life of the metal.

The attempt to develop hot-air engines on a large scale has been abandoned; and except for engines of insignificant size, motors of this class are obsolete.

198. Internal Combustion Engines.—The opposing conditions involved in hot-air engines are completely obviated by the method of heating by internal combustion. The rapid chemical action supported by the medium itself makes possible the rapid heating of large quantities of air to a very high temperature. The medium and the furnace being within the cylinder, the outer surface of the metal walls can be kept at low temperature by cold water circulated in a jacket, and consequently the inner surface can be exposed to the high temperature desired without danger of destruction. Furthermore, the low conductivity of gases becomes here an advantage as it prevents a rapid flow of heat from the medium to the cylinder walls. The low gas temperature of the hot-air engine results in a small effective pressure, and the engine is consequently very bulky for the power obtained. The high temperature possible in the internal combustion motor, on the other hand, permits high effective pressures, and the engine has therefore a relatively small bulk per horsepower.

The first internal combustion engine that attained commercial success was the Lenoir engine patented in France in 1860. In

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structure the Lenoir engine resembled a steam engine with separate slide valves for admission and exhaust. The mixture of gas and air was drawn into the cylinder for about one-half of the stroke, then the admission valve was closed and the charge was ignited by a spark. On the return stroke the products of combustion were discharged while a charge was admitted to the other end of the cylinder.

In the Lenoir engine the charge of air and gas was not compressed before explosion. The necessity of compression as a requisite for high efficiency was recognized by several inventors and in a patent taken out in Paris in 1862 Beau de Rochas stated clearly the conditions required for high efficiency and the cycle of operations that should be executed by the engine. The Otto "silent" engine brought out in 1876 used the Beau de Rochas cycle, which is as follows.

1. Suction of the mixture of fuel and air into the cylinder during the first stroke of the piston.

2. Compression of this mixture during the second stroke.

3. Ignition at the dead point and expansion of the products of combustion during the third stroke.

4. Discharge of the burned gases from the cylinder during the fourth and last stroke.

The Beau de Rochas or Otto cycle, thus described, is the one used at the present time by all internal combustion engines of the explosive type.

Clerk in 1880 introduced the *two-cycle* engine, in which the four operations of the Otto cycle are completed in two strokes of the working piston.

Brayton (1872–1874) was the first to introduce the principle of slow burning of the fuel. In the Brayton oil engine compressed air flowed from a compressor into the power cylinder and on its way through the valve became mixed with the vapor of gasoline or kerosene. The mixture on entering the cylinder was ignited by a flame and the combustion proceeded at practically constant pressure during the period of admission.

The Diesel engine invented by Rudolf Diesel in 1893 also uses the slow-burning method. Air alone is admitted to the cylinder during the suction stroke and on the return stroke is compressed to a high pressure so that the temperature attained

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is higher than the ignition temperature of the fuel. At the beginning of the third stroke liquid fuel is injected and burns at nearly constant pressure during the period of admission. Then follows the expansion and discharge of the burned gases as in the Otto cycle.

During the early years of the period of development of the internal combustion engine illuminating gas was used as a fuel and only engines of small size were constructed. With the introduction of producer gas, a much cheaper fuel, engines of greater power were constructed, and at present installations of gas engines exceeding 5000 brake horse power are not uncommon. Oil engines of the Diesel type are now used quite extensively in marine service.

199. Fuels.—Any combustible gas may be used as a fuel in the internal combustion engine. The following are the gases commonly used.

1. Natural gas.
2. Manufactured gases { Illuminating gas. / Producer gas.
3. By-product gases { Coke-oven gas. / Blast-furnace gas.

Natural gas where obtainable is an excellent fuel. It has a high heating value, its chief constituent being methane, CH_4. Illuminating gas is also a rich gas, but on account of its high cost is used for small engines only. Producer gas is formed by the incomplete combustion of coal. It consists chiefly of carbon monoxide and nitrogen and has a low heating value; it is used extensively for internal combustion engines. Blast furnace gas is essentially a producer gas obtained as a by-product in metallurgical processes.

The liquid fuels used by internal combustion engines are for the most part petroleum products—gasoline, kerosene, fuel oil. The alcohols C_2H_6O and CH_4O make satisfactory fuels but are not much used on account of cost.

200. Operation of Internal Combustion Engines.—The cycle of the modern internal combustion engine involves three changes of state.

1. Compression of the mixture of fuel and air required for

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combustion. On the indicator diagram, Fig. 104, this change is represented by the curve AB, which in the ideal case is an adiabatic. Compression is essential for high efficiency.

2. Combustion of the fuel with an accompanying increase of temperature and pressure, as shown by the curve BC. The character of the combustion depends upon the way in which the fuel is mixed with air. In the case of the Otto engine the fuel and air are mixed before entering the engine cylinder and the mixture is compressed. Upon ignition, therefore, the combustion is so rapid as to constitute an explosion and the combustion curve BC is nearly vertical at the beginning of the expansion stroke. In this case we may assume that the combustion is at constant volume.

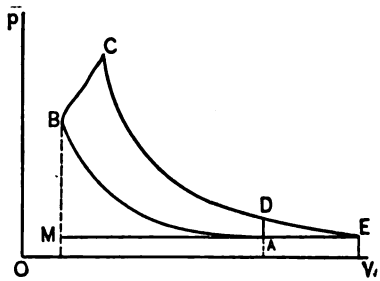


Fig. 104.

The Diesel engine employs a different system of operation. Air without fuel is admitted to the cylinder and compressed. The compression is carried to about 500 lb. per sq. in., which is much higher than is possible with the Otto engine. Adiabatic compression to this pressure gives a final temperature of 1100° to 1400° F., which is higher than the ignition temperature of the fuel. Into this air, in the state represented by point B, liquid fuel is injected during a part of the piston stroke. The particles of fuel immediately ignite and burn and the combustion proceeds as long as the fuel is admitted. The course of the combustion curve BC depends upon the rate of admission of the fuel but in practice the combustion is practically at constant pressure.

3. The mixture of products of combustion expand, as indicated by the curve CD. Under ideal conditions the expansion is adiabatic; in the actual operation, however, heat is rejected to a water jacket during the process. Usually the final volume at the end of expansion is the same as the volume of the charge at the beginning of compression; that is, point D is vertically above point A. Attempts have been made, however, to carry the expansion to point E, at which the pressure is, the same as the original pressure at point A.

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To give the necessary changes of state four strokes of the piston are usually required for each cycle.

1. The *suction stroke* in which the mixture of air and fuel (or air alone) is drawn into the cylinder at nearly atmospheric pressure. During this stroke the indicator pencil draws the line MA.

2. The *compression stroke*, during which the charge in the cylinder is compressed, as indicated by curve AB.

3. The *expansion stroke*, during which the fuel is burned and the products of combustion expand.

4. The *discharge stroke*, in which the products mixture is discharged from the cylinder. In the indicator, diagram DA represents the fall of pressure as the medium rushes out of the cylinder upon the opening of the exhaust valve, and AM represents the discharge of the remaining products at constant pressure. Engines operating on the Otto system may be so arranged as to complete the cycle in two working strokes instead of four.

201. Efficiency of Internal Combustion Engines.—With the assumption of certain ideal conditions, an expression for the efficiency of the internal combustion engine is readily derived. We consider in the first place engines having the indicator diagram $ABCD$, Fig. 104, in which the volumes indicated by points A and D are equal. In this cycle the process represented by DA involves no external work, hence the work (W) of the cycle is

$$(W) = {}_AW_B + {}_BW_C + {}_CW_D. \tag{1}$$

Evidently (W) is represented by the area $ABCD$. For the ideal case we assume that the three processes AB, BC, and CD are adiabatic. Such being the case, the work delivered during the three processes is equal to the decrease of energy; that is

$$A({}_AW_B + {}_BW_C + {}_CW_D) = U_A - U_D, \tag{2}$$

or from (1)

$$A(W) = U_A - U_D. \tag{3}$$

Let the subscripts 1, 2, 3, 4 indicate the states A, B, C, D; and further let the subscript m apply to the original mixture of air and fuel and the subscript p to the mixture of products.

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Since at A we have the fuel mixture and at D the products mixture, (3) may be written in this new notation

$$A(W) = U_{m1} - U_{p4}, \tag{4}$$

the first subscript denoting the character of the mixture, and the second the state. This equation may be modified by adding and subtracting U_{p1}; thus

$$A(W) = U_{m1} - U_{p1} - (U_{p4} - U_{p1}). \tag{5}$$

Let M denote the weight of mixture present and M' the weight of fuel in the original mixture; then

$$U_{m1} - U_{p1} = M(u_{m1} - u_{p1}) = M'H_v$$

and $$U_{p4} - U_{p1} = M(u_{p4} - u_{p1}).$$

Therefore (5) becomes

$$A(W) = M'H_v - M(u_{p4} - u_{p1}). \tag{6}$$

If now we take the heating value $M'H_v$ of the fuel at the temperature T_1 as the energy supplied by the combustion, the efficiency is

$$\eta = \frac{A(W)}{M'H_v} = 1 - \frac{u_{p4} - u_{p1}}{\frac{M'}{M} H_v}. \tag{7}$$

From (16), Art. 192,

$$u_{p4} - u_{p1} = a_p(T_4 - T_1) + \tfrac{1}{2}b_p(T_4^2 - T_1^2) + \tfrac{1}{3}f_p(T_4^3 - T_1^3). \tag{8}$$

We have therefore the important result that the efficiency depends upon the temperature T_4 at the end of adiabatic expansion. If by changing the compression or the character of the combustion the temperature T_4 can be lowered the efficiency will thereby be increased. The course of the curve BC, representing the change of state during combustion, has no influence on the efficiency except as it affects the final temperature T_4.

We investigate now the cycle $ABCE$, in which the expansion is prolonged until the original pressure p_1 is reached. Let the subscript 4 apply now to the state E. In this case the work delivered is

$$(W) = {}_AW_B + {}_BW_C + {}_CW_E + {}_EW_A \tag{9}$$

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The three processes AB, BC, and CE being adiabatic, we have as before

$$A({}_AW_B + {}_BW_C + {}_CW_E) = U_A - U_E = U_{m1} - U_{p4}; \quad (10)$$

also

$${}_EW_A = -p_A(V_E - V_A) = (p_1V_1 - p_4V_4). \quad (11)$$

Hence $$A(W) = U_{m1} - U_{p4} + A(p_1V_1 - p_4V_4) \quad (12)$$

But $$U_{m1} + Ap_1V_1 = I_{m1} = Mi_{m1},$$

and $$U_{p4} + Ap_4V_4 = I_{p4} = Mi_{p4}.$$

Therefore (12) may be written

$$A(W) = M(i_{m1} - i_{p4}),$$

or $$A(W) = M(i_{m1} - i_{p1}) - M(i_{p4} - i_{p1}). \quad (13)$$

The difference $i_{m1} - i_{p1}$ is however the heating value at constant pressure of unit weight of the fuel at the temperature T_1; hence

$$M(i_{m1} - i_{p1}) = M'H_p,$$

and

$$A(W) = M'H_p - M(i_{p4} - i_{p4}). \quad (14)$$

In this case we may take the heating value $M'H_p$ as the energy supplied, and the expression for efficiency is

$$\eta = 1 - \frac{i_{p4} - i_{p1}}{\frac{M'}{M}H_p}. \quad (15)$$

From (20), Art. 192, the numerator of the fraction is

$$i_{p4} - i_{p1} = a_p'(T_4 - T_1) + \tfrac{1}{2}b_p(T_4^2 - T_1^2) + \tfrac{1}{3}f_p(T_4^3 - T_1^3).$$

202. The Ideal Otto Cycle.—The efficiency of the ideal Otto cycle furnishes a basis for estimating the performance of an internal combustion engine of the explosive type just as the Rankine cycle serves the same purpose in the case of the steam engine.

Assuming in this ideal case that no heat is rejected to the surroundings, the efficiency is given by (7) of the preceding article. In the calculation of this efficiency the temperature T_4 must be found; and this, in turn, involves the determination of the intermediate temperatures T_2 and T_3.

The initial temperature T_1 and the two pressures p_1 and p_2 are

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supposed to be known. Then the temperature T_2 is given by equation (9) of Art. 189, namely

$$(a_m + AB_m)\log_e \frac{T_2}{T_1} + b_m(T_2 - T_1) + \tfrac{1}{2}f_m(T_2^2 - T_1^2) = AB_m \log_e \frac{p_2}{p_1}. \quad (1)$$

If the fuel mixture contains no CO_2 the coefficient f_m is zero.

The determination of the temperature T_3 would be difficult if the combustion curve followed some arbitrary course as shown in Fig. 104. In the case of the ideal Otto cycle, however, we assume that the combustion line is vertical, as 2–3 Fig. 105. Since there is no change of volume ${}_2W_3 = 0$, and since the process is adiabatic ${}_2Q_3 = 0$; hence there is no change of energy, and

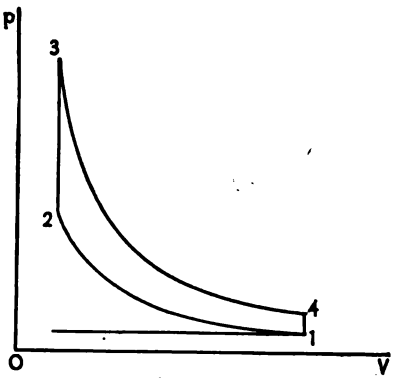


FIG. 105.

$$U_3 = U_2.$$

The energy of the fuel mixture at temperature T_2 is

$$u_2 = u_{m0} + a_m T_2 + \tfrac{1}{2}b_m T_2^2 + \tfrac{1}{3}f_m T_2^3,$$

and the energy of the products mixture at temperature T_3 is

$$u_3 = u_{p0} + a_p T_3 + \tfrac{1}{2}b_p T_3^2 + \tfrac{1}{3}f_p T_3^3.$$

Therefore we have (taking $u_{m0} - u_{p0} = \frac{M'}{M}H_0$),

$$a_p T_3 + \tfrac{1}{2}b_p T_3^2 + \tfrac{1}{3}f_p T_3^3 = \frac{M'}{M}H_0 + a_m T_2 + \tfrac{1}{2}b_m T_2^2 + \tfrac{1}{3}f_m T_2^3. \quad (2)$$

and from this relation the temperature T_3 is determined.

The pressure p_3 is found from the two equations

$$p_2 v_2 = B_m T_2, \qquad p_3 v_3 = B_p T_3.$$

Since $v_3 = v_2$, combination of these equations gives

$$p_3 = p_2 \frac{B_p}{B_m}\frac{T_3}{T_2}. \quad (3)$$

Finally, the temperature T_4 is determined by the application of

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equation (8) Art. 189, to the adiabatic expansion 3–4. Changing the subscripts, the equation is

$$a_p \log_e \frac{T_4}{T_3} + b_p(T_4 - T_3) + \tfrac{1}{2} f_p(T_4^2 - T_3^2) = AB_p \log_e \frac{v_3}{v_4}. \quad (4)$$

EXAMPLE. Determine the efficiency of the ideal Otto engine under the following conditions. The fuel used is the producer gas whose composition was given in Art. 186, and the gas is burned with 20 per cent. excess of air. The pressure at the beginning of compression is 14.7 lb. per sq. in., and at the end of compression it is 150 lb. per sq. in. The temperature at the beginning of compression is 190° F., or $T_1 = 650°$.

The two mixtures are given in the following schedules. See Art. 191.

	Fuel and air				Mixture of Products		
	Mols	m	Lb.		Mols	m	Lb.
H_2	0.09	2	0.18	CO_2	0.32	44	14.08
CO	0.24	28	6.72	H_2O	0.13	18	2.34
CH_4	0.02	16	0.32	O_2	0.041	32	1.312
CO_2	0.06	44	2.64	N_2	1.525	28	42.70
O_2	0.246	32	7.872		2.016		60.432
N_2	1.525	28	42.70				
	2.181		60.432				

From these schedules the necessary constants are determined. Thus

$$M' = 0.18 + 6.72 + 0.32 = 7.22, \quad M = 60.432, \quad \frac{M'}{M} = 0.1195,$$

$$B_m = \frac{1544 \times 2.181}{60.432} = 55.72, \quad AB_m = 0.07166,$$

$$B_p = \frac{1544 \times 2.016}{60.432} = 51.51, \quad AB_p = 0.06624.$$

In the original mixture the diatomic gases H_2, CO, O_2 and N_2 aggregate 2.101 mols, and in the products mixture 1.566 mols. Taking the formulæ for the molecular specific heats at constant volume the specific heat coefficients are calculated as follows:

$$a_m = \frac{2.101 \times 4.66 + 0.02 \times 1.34 + 0.06 \times 5.23}{60.432} = 0.16765,$$

$$b_m = \frac{2.101 \times 0.5 + 0.02 \times 9 + 0.06 \times 3.7}{60.432 \times 10^3} = 2.404 \times 10^{-5},$$

$$f_m = -\frac{0.06 \times 0.528}{60.432 \times 10^6} = -5.24 \times 10^{-10},$$

$$a_p = \frac{0.32 \times 5.23 + 0.13 \times 5.13 + 1.566 \times 4.66}{60.432} = 0.1595,$$

$$b_p = \frac{0.32 \times 3.7 + 0.13 \times 1.44 + 1.566 \times 0.5}{60.432 \times 10^1} = 3.565 \times 10^{-5},$$

$$f_p = \frac{-0.32 \times 0.528 + 0.13 \times 0.125}{60.432 \times 10^6} = -25.27 \times 10^{-10}.$$

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The lower heating value is obtained from the following schedule.

	Lb.	H_v per lb.	Product
H_2.....	0.18	52,930	9,527.4
CO.....	6.72	4,380	29,433.6
CH_4.....	0.32	21,670	6,934.4
			45,895.4

Dividing this sum by the total weight, 60.432 lb., we get

$$\frac{M'}{M} H_v = \frac{45895.4}{60.432} = 759.5 \text{ B. t. u.}$$

Taking 62° F. as the standard temperature associated with this heating value, the constant $\frac{M'}{M} H_0$ and the heating value $\frac{M'}{M} H_v$ at $T_1 = 650°$ may be determined from the equations in Art. 193. We find

$$\frac{M'}{M} H_0 = 758.1 \text{ B. t. u.}, \left[\frac{M'}{M} H_v\right]_{T=650} = 759.1 \text{ B. t. u.}$$

To determine the temperature T_2 at the end of compression, we have equation (1), which becomes when the numerical values are inserted

$$0.2393 \log_e \frac{T_2}{T_1} + 2.404 \times 10^{-5}(T_2 - 650) - 2.62 \times 10^{-10}(T_2^2 - 650^2) = 0.07166 \log_e \frac{150}{14.7}.$$

Dividing by 0.2393 and by 2.3026, this equation is reduced to the form

$$\log T_2 + [5.63977]T_2 - [10.67714]T_2^2 = 3.14316,$$

and by trial the value $T_2 = 1231$ is found.

To find the temperature T_3 we substitute known values in (2) and thus obtain

$$0.1595T_3 + 1.7825 \times 10^{-5}T_3^2 - 8.423 \times 10^{-10}T_3^3 = 758.1 + 0.16765 \times 1231 + 1.202 \times 10^{-5} \times 1231^2 - 1.75 \times 10^{-10} \times 1231^3 = 976.9$$

From this equation $T_3 = 4407$. The pressure p_3 is found from a combination of the equations $p_2v_2 = B_mT_2$, $p_3v_3 = B_pT_3$, whence, since $v_3 = v_2$,

$$p_3 = p_2 \frac{B_p}{B_m} \frac{T_3}{T_2} = 150 \times \frac{51.51}{55.72} \times \frac{4407}{1231} = 496.4 \text{ lb. per sq. in.}$$

The ratio of the volumes v_1 and v_2 is obtained from the equation

$$\frac{v_1}{v_2} = \frac{p_2}{p_1} \frac{T_1}{T_2} = \frac{150}{14.7} \times \frac{650}{1231} = 5.388 \qquad \left[\log \frac{v_1}{v_2} = 0.73142\right]$$

The temperature T_4 is found from (4). The ratio $\frac{v_4}{v_3}$ is equal to the ratio $\frac{v_1}{v_2}$. Substituting the known values in (4) and reducing the equation to its simplest form, we have

$$\log T_4 + [5.98708]T_4 - [9.53660]T_4^2 = 3.70134,$$

from which $T_4 = 2840$.

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The work in B. t. u. per pound of mixture is

$$A(W) = 759.1 - [0.1595(2840 - 650) + 1.7825 \times 10^{-5}(2840^2 - 650^2) - 8.423 \times 10^{-10}(2840^3 - 650^3)] = 292.6 \text{ B. t. u.},$$

and the efficiency is

$$\eta = \frac{292.6}{759.1} = 0.385.$$

203. The Ideal Diesel Cycle.—The analysis of the Diesel cycle is complicated by the fact that the weight of medium is not the same throughout the cycle. As usual, let M' denote the weight of the fuel, M the weight of fuel and air, and therefore $M - M'$ the weight of the air alone; then during the compression 1–2, Fig. 106, the weight $M - M'$ is present and during the expansion 3–4 the weight of the products is M.

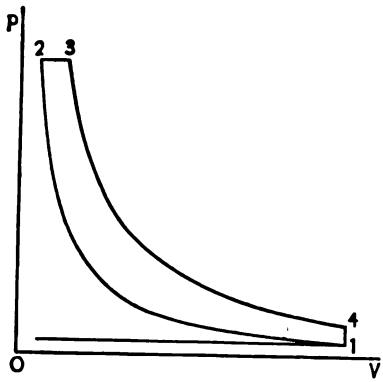


Fig. 106.

The three changes 1–2, 2–3, 3–4 are assumed to be adiabatic. Therefore

$$A_1W_2 = U_1 - U_2 = (M - M')(u_{m1} - u_{m2}); \quad (1)$$

$$A_3W_4 = U_3 - U_4 = M(u_{p3} - u_{p4}). \quad (2)$$

The work obtained during the combustion process 2–3 is likewise equal to the decrease of energy, but the energy of the fuel must be taken into account. Denoting by u' the energy of unit weight of the oil, the energy of the fuel is $M'u'$; hence

$$A_2W_3 = (M - M')u_{m2} + M'u' - Mu_{p3}. \quad (3)$$

Adding the three equations, we have

$$A(W) = (M - M')u_{m1} + M'u' - Mu_{p4}, \quad (4)$$

or

$$A(W) = [(M - M')u_{m1} + M'u' - Mu_{p1}] - M(u_{p4} - u_{p1}). \quad (5)$$

The term in brackets is evidently the heat rejected in burning at constant volume M' lb. of fuel with $M - M'$ lb. of air; that is, it is the heating value $M'H_v$ at temperature T_1. Hence (5) may be written

$$A(W) = M'H_v - M(u_{p4} - u_{p1}). \quad (6)$$

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Equation (3) gives one expression for the work ${}_2W_3$; we have also

$$ {}_2W_3 = p_3V_3 - p_2V_2, $$

and therefore

$$ (M - M')u_{m2} + M'u' - Mu_{p3} = A(p_3V_3 - p_2V_2). \quad (7) $$

However, we have

$$ p_2V_2 = (M - M')p_2v_2, $$
$$ p_3V_3 = Mp_3v_3, $$

and (7) may be written

$$ (M - M')\,(u_{m2} + Ap_2v_2) + M'u' - M(u_{p3} + Ap_3v_3) = 0 $$

or

$$ (M - M')i_{m2} + M'u' - Mi_{p3} = 0. \quad (8) $$

Adding and subtracting Mi_{p2}, (8) may be written

$$ (M - M')i_{m2} + M'u' - Mi_{p2} = M(i_{p3} - i_{p2}). $$

The first member of this equation is approximately the heating value $M'H_p$ at the temperature T_2; hence

$$ M'H_p]_{T2} = M(i_{p3} - i_{p2}) $$

or

$$ \frac{M'}{M}H_p\Big]_{T_2} = a'_p(T_3 - T_2) + \tfrac{1}{2}b_p(T_3^2 - T_2^2) + \tfrac{1}{3}f_p(T_3^3 - T_2^3). \quad (9) $$

Having the initial conditions, p_1 and T_1, and the pressure p_2, the temperature T_2 is found as in the case of the Otto cycle, using the constants for air. Then the temperature T_3 is found from (9), and finally the temperature T_4 from (4) of the preceding article. The volume v_3 is readily obtained from the two equations

$$ p_2v_2 = (M - M')B_mT_2, \quad p_3v_3 = MB_pT_3, $$

whence

$$ \frac{v_3}{v_2} = \frac{M}{M - M'}\frac{B_p}{B_m}, \quad (10) $$

in which B_m is the constant for air.

Three heating values come into consideration in the preceding analysis; H_v and H_p at temperature T_1, and H_p at temperature T_2. If an accurate value of any one of these is available, the other two may be calculated; however, the difference between H_v and H_p is small in any case, and as the heating values of liquid fuels are not well established, it is permissible to take the same

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value for all three. The heating value $M'H_p$ at temperature T_1 appears to be the consistent measure of the energy supplied. From (6), therefore, the efficiency of the ideal cycle is

$$\eta = \frac{A(W)}{M'H_p} = \frac{H_v}{H_p} - \frac{u_{p4} - u_{p1}}{\frac{M'}{M}H_p},$$

or taking $H_v = H_p$,

$$\eta = 1 - \frac{u_{p4} - u_{p1}}{\frac{M'}{M}H_p} \tag{11}$$

Hence the efficiency of the Diesel cycle is given by the same expression as the efficiency of the Otto cycle.

EXAMPLE. Find the ideal efficiency of a Diesel engine operating under the following conditions. The fuel is oil having approximately the composition C = 0.845, H = 0.155 by weight, and a heating value of 18,600 B. t. u. per pound; 19 lb. of air per pound of fuel; $p_1 = 14.7$, $p_2 = 500$ lb. per sq. in.; and $T_1 = 650°$ F.

The theoretical weight of oxygen required per pound of fuel is

$$0.845 \times \frac{32}{12} + 0.155 \times \frac{16}{2} = 3.493 \text{ lb.}$$

Taking 0.231 lb. of oxygen per pound of air, the theoretical weight of air per pound of oil is $3.493 \div 0.231 = 15.121$ lb.; hence, the excess of air is $19 - 15.121 = 3.879$ lb., and the excess of oxygen is $3.879 \times 0.231 = 0.986$ lb. The nitrogen in 19 lb. of air is $19 \times 0.769 = 14.611$ lb. The weight of CO_2 formed is $0.845 \times \frac{44}{12} = 3.098$ lb., and the weight of H_2O formed is $0.155 \times 9 = 1.395$ lb. The composition of the products mixture is, therefore

	Lb.	Mols
CO_2	3.098	0.0704
H_2O	1.395	0.0775
O_2	0.896	0.0280
N_2	14.611	0.5218
	20.0	0.6977

The constants of the air and of the products mixture are readily obtained. They are as follows:

Air	Products
$B_m = 53.34$	$B_p = 53.86$
$AB_m = 0.0686$	$AB_p = 0.0693$
$a_m = 0.1611$	$a_p = 0.1664$
$b_m = 1.727 \times 10^{-5}$	$b_p = 3.235 \times 10^{-5}$
$f_m = 0$	$f_p = -13.74 \times 10^{-10}$
$a_m + AB_m = 0.2297$	$a_p + AB_p = 0.2357$

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The temperature T_2 is obtained from the equation

$$0.2297 \log_e \frac{T_2}{650} + 1.727 \times 10^{-5}(T_2 - 650) = 0.0686 \log_e \frac{500}{14.7},$$

from which $T_2 = 1720$.

Taking $\frac{M'}{M} H = \frac{1}{20} \times 18{,}600 = 930$, equation (9) becomes

$$930 = 0.2357(T_3 - 1720) + 1.6175 \times 10^{-5}(T_3^2 - 1720^2) - 4.58 \times 10^{-10}(T_3^3 - 1720^3)$$

This equation is satisfied by the value $T_3 = 4597$.

The volume ratio $\frac{V_4}{V_3}$ is required in the equation for the adiabatic expansion. Since $V_4 = V_1$, this ratio may be found by a comparison of states 1 and 3, bearing in mind that at state 1 the weight of medium is 19 lb., while at state 3 it is 20 lb. From the equations

$$p_1 V_1 = 19 B_m T_1, \; p_3 V_3 = 20 B_p T_3,$$

we have

$$\frac{V_1}{V_3} = \frac{V_4}{V_3} = \frac{19}{20} \cdot \frac{53.34}{53.86} \cdot \frac{650}{4597} \cdot \frac{500}{14.7} = 4.525. \; [\log \frac{V_4}{V_3} = 0.65559]$$

Substituting the known values in the equation for the adiabatic expansion of the products, the resulting equation after reduction is

$$\log T_4 + [\bar{5}.92650] \; T_4 - [\bar{9}.26359] \; T_4^3 = 3.73880$$

and the value of T_4 is found to be 3116.

The work delivered per pound of medium is

$$930 - [0.1664(3116 - 650) + 1.6175 \times 10^{-5}(3116^2 - 650^2) - 4.58 \times 10^{-10}(3116^3 - 650^3) = 383.2 \text{ B. t. u.}$$

and the efficiency is, accordingly,

$$\eta = \frac{383.2}{930} = 0.412$$

204. Air-Standard Efficiency.—In works on the internal combustion engine it is customary to base the performance of the engine on the so-called *air-standard*. The medium throughout the cycle is assumed to be air, and the specific heat is taken as constant. It is assumed that during the change of state 2–3, Fig. 105, an amount of heat equal to the heat of combustion is absorbed by the air from external sources; and that 4–1, Fig. 105, represents rejection of heat at constant volume.

With these assumptions the efficiency of the Otto cycle is readily determined. The heat absorbed is

$$_2Q_3 = Mc_v(T_3 - T_2),$$

the heat rejected is

$$_4Q_1 = Mc_v(T_4 - T_1),$$

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and the heat transformed into work is

$$A(W) = Mc_v(T_3 - T_2) - Mc_v(T_4 - T_1).$$

The efficiency is therefore

$$\eta = \frac{A(W)}{{}_2Q_3} = 1 - \frac{T_4 - T_1}{T_3 - T_2}. \tag{1}$$

Since the changes 1–2 and 3–4 are adiabatic, we have

$$\left(\frac{v_2}{v_1}\right)^{k-1} = \frac{T_1}{T_2}, \quad \left(\frac{v_3}{v_4}\right)^{k-1} = \frac{T_4}{T_3},$$

whence

$$\frac{T_4}{T_3} = \frac{T_1}{T_2}.$$

The expression for the efficiency reduces therefore to

$$\eta = 1 - \frac{T_1}{T_2}, \tag{2}$$

or

$$\eta = 1 - \left(\frac{p_1}{p_2}\right)^{\frac{k-1}{k}} \tag{3}$$

For the Diesel cycle,

$${}_2Q_3 = Mc_p(T_3 - T_2)$$

$${}_4Q_1 = Mc_v(T_2 - T_1)$$

$$A(W) = Mc_p(T_3 - T_2) - Mc_v(T_4 - T_1)$$

and

$$\eta = 1 - \frac{T_4 - T_1}{k(T_3 - T_2)}, \tag{4}$$

Referring to the example of Art. 202, the air-standard efficiency is

$$\eta = 1 - \left(\frac{14.7}{150}\right)^{\frac{0.4}{1.4}} = 0.485.$$

which may be compared with 0.385 the efficiency obtained by the more accurate analysis. Actual engines working under the conditions stated in this example have shown efficiencies of about 0.30. If the air-standard is taken as the basis of comparison, the efficiency referred to this standard is 0.30 : 0.485, or about 62 per cent. This figure is misleading and unjust to the engine. Comparing the efficiency actually attained with the efficiency 0.385, which is the highest possible under the conditions, it appears that the engine utilizes nearly 80 per cent. of the available energy.

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205. Effects of Loss of Heat to Jacket.—The ideal condition of adiabatic changes throughout the cycle cannot be attained in practice. In order that the inner walls of the cylinder shall be maintained at a sufficiently low temperature, there must be a steady flow of heat from the gases inside the cylinder to a medium surrounding the cylinder, either water or air. Tests of engines show that heat equivalent to 30 per cent. or more of the heating value of the fuel is thus rejected. The result is a reduction of the pressures and temperatures from those calculated on the assumption of adiabatic conditions. If the amount of heat rejected is known the modified temperatures and pressures and the efficiency under the conditions may be calculated, at least approximately.

Let q_c denote the heat rejected per unit weight of medium during the combustion phase 2–3, and q_e the heat rejected during the expansion 3–4. In the case of the Otto cycle we still assume that the combustion is at constant volume; hence the energy equation gives

$$-q_c = u_3 - u_2, \tag{1}$$

or

$$u_3 = u_2 - q_c.$$

Hence equation (2), Art. 202, becomes

$$a_p T_3 + \tfrac{1}{2} b_p T_3^2 + \tfrac{1}{3} f_p T^3_3 = \left(\frac{M'}{M} H_o - q_c\right) + a_m T_2 + \tfrac{1}{2} b_m T_2^2 + \tfrac{1}{3} c_m T^3_2. \tag{2}$$

That is, $\frac{M'}{M} H_o$ in the original equation is replaced by $\frac{M'}{M} H_o - q_c$.

The energy equation applied to the expansion 3–4 is

$$-q_e = u_4 - u_3 + A_3 W_4. \tag{3}$$

The expansion curve on the pv-plane, with or without the flow of heat, may be represented quite exactly by the equation $pv^n = \text{const.}$ The value of n depends upon the amount of heat rejected. Assuming that this equation is valid, the work of expansion per pound of medium is given by the expression

$${}_3W_4 = \int_{v_3}^{v_4} p\,dv = \frac{p_3 v_3 - p_4 v_4}{n-1} = \frac{B_p}{n-1}(T_3 - T_4). \tag{4}$$

Substituting in (3), the result is

$$-q_e = u_4 - u_3 + \frac{AB_p}{n-1}(T_3 - T_4),$$

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and inserting the usual expressions for u_3 and u_4, we obtain the equation

$$q_e = \left(a_p - \frac{AB_p}{n-1}\right)(T_3 - T_4) + \tfrac{1}{2}b_p(T_3^2 - T_4^2) + \tfrac{1}{3}f_p\,(T_3^3 - T_4^3). \quad (5)$$

From the equation $pv^n = \text{const.}$, we have also

$$\frac{T_3}{T_4} = \left(\frac{v_4}{v_3}\right)^{n-1}$$

or

$$n - 1 = \frac{\log T_3 - \log T_4}{\log v_4 - \log v_3}. \quad (6)$$

From equations (5) and (6) the values of the two unknown quantities n and T_4 may be calculated. In making this calculation choose several values of T_4, as 2000, 2220, 2400, etc. and find from (5) the corresponding values of $n - 1$; then for the same temperatures calculate from (6) values of $n - 1$; plot the two curves for $n - 1$ as a function of T_4; and observe the intersection.

Let $q_r = q_c + q_e$ denote the total heat rejected per pound of medium. Then the work per cycle is obtained from equation (6), Art. 201, with q_r subtracted; thus

$$A(W) = M'H_v - M(u_{p4} - u_{p1}) - Mq_r. \quad (7)$$

The efficiency is, therefore

$$\eta = 1 - \frac{(u_{p4} - u_{p1}) + q_r}{\frac{M'}{M}H_v}. \quad (8)$$

EXAMPLE. In the example of Art. 202, assume that the heat rejected to the jacket is about 30 per cent. of the heating value. The distribution of this loss between the combustion and expansion phases is not well known; but we may assign about 9 per cent. to the combustion process and the remaning 21 per cent. to the expansion. Then

$q_r = 759.1 \times 0.30 = 228$ B. t. u. approx.
$q_c = 759.1 \times 0.09 = 68$ B. t. u.
$q_e = 160$ B. t. u.

The small loss of heat during compression may be neglected, and with adiabatic compression $T_2 = 1231$, as in the original solution. For the temperature T_3 we have

$0.1595T_3 + 1.7825 \times 10^{-5}T_3^2 - 8.423 \times 10^{-10}T_3^3 = 976.9 - 68 = 908.9$,

from which $T_3 = 4151$.

From (5) and (6) we now find the following values of T_4 and n: $T_4 = 2127$, $n = 1.397$.

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We have, therefore,

$$u_{p4} - u_{p1} + q_r = a_p(T_4 - T_1) + \tfrac{1}{2}b_p(T_4^2 - T_1^2) + \tfrac{1}{3}f_p(T_4^3 - T_1^3) + q_r$$
$$= 0.1595(2127 - 650) + 1.7825 \times 10^{-5}(2127^2 - 650^2) - 8.423 \times 10^{-10}(2127^3 - 650^3) + 228$$
$$= 528.8$$

and the efficiency is

$$\eta = 1 - \frac{528.8}{759.1} = 0.303.$$

206. Maximum Pressures.—The problem of the determination of the maximum pressure at the end of combustion has received much attention on the part of writers on the internal combustion engine; and various theories have been advanced to account for an apparent discrepancy between the calculated pressure and the pressure actually attained as shown by the indicator diagram. Some light may be thrown on this supposed discrepancy by the calculation of the maximum pressure in a specific instance with various assumptions as to the conditions.

Let the preliminary data of the example of Art. 202 be taken; that is, $p_1 = 14.7$ lb., $p_2 = 150$ lb., $T_1 = 650$, $\frac{M'}{M}H_v = 759.5$ B. t. u.

1. Assume the conditions of the air standard. The compression is adiabatic; the combustion is at constant volume, and the heat 759.5 B. t. u. is absorbed by air at constant specific heat, $c_v = 0.17$.

The temperature at the end of compression is

$$T_2 = T_1\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} = 650\left(\frac{150}{14.7}\right)^{\frac{0.4}{1.4}} = 1262.$$

For the temperature T_3, we have

$$\frac{M'}{M}H_v = c_v(T_3 - T_2)$$

or $$T_3 = T_2 + \frac{1}{c_v}\frac{M'}{M}H_v = 1262 + \frac{759.5}{0.17} = 5730.$$

Since the air is heated at constant volume, we have

$$\frac{p_3}{p_2} = \frac{T_3}{T_2}, \quad p_3 = 150 \times \frac{5730}{1262} = 681 \text{ lb. per sq. in.}$$

2. Assume the conditions stated in Art. 202. The pressure p_3 was found to be 496.4 lb. per sq. in. Thus by taking account

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of the variation of specific heat with the temperature the calculated pressure is reduced from 681 lb. to 496.4 lb.

3. Assume that heat is lost to the water in the jacket, as in the example of Art. 205. The temperature T_3 was found to be 4151° absolute; with the other conditions remaining the same, the pressure p_3 is in this case

$$p_3 = 496.4 \times \frac{4151}{4407} = 467.6 \text{ lb. per sq. in.}$$

4. In the preceding cases it has been assumed that the combustion has proceeded at constant volume; that is, the combustion line 2–3 is parallel to the v-axis, as shown in Fig. 105. Indicator diagrams in some instances show this condition, but usually the time required for combustion is such that the combustion line has somewhat the form shown in Fig. 107. Deviation of the combustion line from the ideal constant volume condition has a marked effect in reducing the maximum pressure p_3. In the first place, the medium during combustion does work represented by the area under the curve 2–3, and as a result the energy of the gas, and consequently the temperature, at state 3 is reduced. Then the increase of the volume v_3 involves a corresponding reduction of pressure.

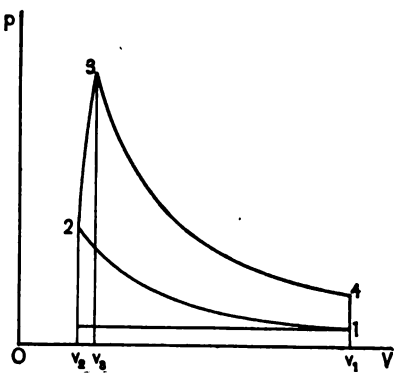


Fig. 107.

Referring to the example of Art. 202, the volume v_1 of one pound of the fuel mixture in the state represented by point 1 is

$$v_1 = 358.7 \times \frac{2.181}{60.432} \times \frac{650}{491.6} = 17.12 \text{ cu. ft.}$$

The volume ratio $v_1 : v_2$ was found to be 5.388; hence $v_2 = 17.12 \div 5.388 = 3.18$ cu. ft., and the volume $v_1 - v_2$ swept through by the piston is $17.12 - 3.18 = 13.94$ cu. ft. The increase of volume $v_3 - v_2$ due to the time required for combustion may be 5 per cent. or more of the displacement volume. Taking 5 per cent. in this case $v_3 - v_2 = 13.96 \times .05 = 0.70$; hence $v_3 = 3.18 +$

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0.70 = 3.88 cu. ft. The pressure p_3 is at present unknown but it is certainly much less than 468 lb. per sq. in. The mean pressure for the combustion curve 2–3 may be taken as $\frac{1}{2}(p_2 + p_3)$, and if p_3 is assumed to lie between 360 and 400 lb., the mean pressure will lie between 250 and 280 lb. Let the mean pressure be taken as 270 lb. per sq. in; then the heat equivalent of the work done during the combustion phase is

$$\frac{270 \times 144 \times 0.70}{778} = 35 \text{ B. t. u.}$$

This amount as well as the 68 B. t. u. given to the jacket water must be subtracted from the heating value $\frac{M'}{M} H_v$. The resulting equation for the determination of T_3 is (see p. 309)

$$0.1595T_3^3 + 1.7825 \times 10^{-5}T_3^2 - 8.423 \times 10^{-10}T_3^3 = 976.9 - 68 - 35 = 873.9$$

and the value $T_3 = 4018$ is obtained. The equations for the determination of T_3 are

$$p_2v_2 = B_mT_2, \qquad p_3v_3 = B_pT_3.$$

Combining these equations, we have

$$p_3 = p_2 \frac{v_2}{v_3} \frac{B_p}{B_m} \frac{T_3}{T_2} =$$

$$150 \times \frac{3.18}{3.88} \times \frac{51.51}{55.72} \times \frac{4018}{1231} = 369.4 \text{ lb. per sq. in.}$$

From the preceding results it is seen that every step towards the actual conditions gives a reduction in the calculated maximum pressure. The pressure 369.4 lb. is slightly less than 2.5 times the compression pressure, which is about the ratio observed in indicator diagrams taken from engines operating with producer gas. When all the conditions are taken into account the calculated pressure agrees very well with the observed pressure

207. Cylinder Volume.—The volume displaced by the piston for a given horse-power and rotative speed is readily calculated. The following example shows the method to be followed.

EXAMPLE. Taking the data already furnished in the examples of Arts. 202, 205, find the cylinder dimensions of a single-cylinder four-cycle engine which at 200 rev. per min. is to develop 80 brake horsepower.

The mechanical efficiency of the engine may be taken as 0.83; hence the maximum indicated horsepower is 80 ÷ 0.83 = 96.4. The heating value

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of the fuel per pound of mixture is 759.5 B. t. u., the efficiency, as calculated in Art. 205, is 0.303. Due to various imperfections in the cycle the actual efficiency will be lower, and the value 0.27 may be assumed. Hence, for one pound of mixture $759.5 \times 0.27 = 205$ B. t. u. is the heat utilized. Since 1 h.p.-min. = 42.44 B. t. u., the weight of mixture required per minute is

$$\frac{42.44 \times 96.4}{205} = 19.95 \text{ lb.}$$

From the example of the preceding article the displacement volume per pound is 13.94 cu. ft., and the displacement per minute is therefore $19.95 \times 13.94 = 278.1$ cu. ft. In the four-cycle engine there are 100 working strokes for 200 r. p. m.; hence the displacement volume per stroke is $278.1 \div 100 = 2.781$ cu. ft. This volume is given by a piston diameter of 16½ in. and a stroke of 22½ in.

In this calculation we have made the assumption that the pressure p_1 at the beginning of compression is 14.7 lb. per sq. in. In practice the suction pressure is lower, and for the type of engine specified it might be taken as 12.5 lb. The displacement volume per pound and the cylinder volume would therefore be increased in the ratio 14.7:12.5. Thus for the required volume, we have

$$2.781 \times \frac{14.7}{12.5} = 3.27 \text{ cu. ft.}$$

and the cylinder dimensions may be 17½ in. diameter by 25 in stroke.

208. Complete Expansion Engines.—The efficiency of the internal combustion engine can be increased by continuing the expansion of the products nearly to atmospheric pressure, as indicated by the curve *CE*, Fig. 104. In this case, the expansion stroke is longer than the effective compression stroke. Two successful engines employing the principle of complete expansion have been placed in operation: the Sargent gas engine and the Humphrey gas pump.

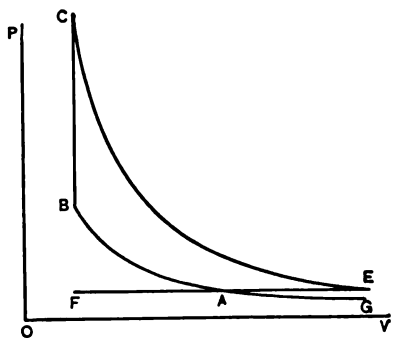


FIG. 108.

The ideal cycle of the Sargent engine is shown in Fig. 108. The line *FA* represents the suction of the charge into the cylinder

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at atmospheric pressure. At about ¾ of the suction stroke the admission valve is closed and for the remainder of the stroke the charge expands adiabatically as shown by curve AG. On the return stroke the charge is compressed, the change being represented by curve GB; then follows the combustion BC and adiabatic expansion CE. Since the path AG is immediately traversed in the opposite direction, it involves no work, and the effective cycle is $ABCE$. As shown in Art. 201, the efficiency of this cycle is given by the expression

$$\eta = 1 - \frac{i_{p4} - i_{p1}}{\frac{M'}{M} H_p}. \tag{1}$$

It is instructive to compare the efficiency of the ideal complete-expansion cycle with that of the ideal Otto cycle. To this end we take the data of the example of Art. 202 and modify the solution to conform to the new conditions.

As before, $T_3 = 1231$, $T_2 = 4407$, and $p_2 = 496.4$ lb. To determine the final temperature T_4 at point E, we have the adiabatic relation

$$a_p \log_e \frac{T_4}{T_2} + b_p(T_4 - T_2) + \tfrac{1}{2} f_p(T_4^2 - T_2^2) = AL_p \log_e \frac{p_4}{p_2},$$

which becomes, with known values inserted

$$0.2257 \log_e \frac{T_4}{4407} + 3.565 \times 10^{-5}(T_4 - 4407) - 12{,}635 \times 10^{-10}(T_4^2 - 4407^2) = 0.06624 \log_e \frac{14.7}{496.4}$$

or $$\log T_4 + [\bar{5}.83631]T_4 - [\bar{9}.38583]T_4^2 = 3.46862,$$

whence $$T_4 = 2150.$$

$$i_{p4} - i_{p1} = 0.2257(2150 - 650) + 1.7825 \times 10^{-5}(2150^2 - 650^2) - 8.423 \times 10^{-10}(2150^3 - 650^3) = 403.2 \text{ B. t. u.}$$

Taking $H_p = H_v$, $\frac{M'}{M} H_p = 759.1$, and the efficiency is

$$1 - \frac{403.2}{759.1} = 0.469.$$

It appears therefore that the ideal efficiency for complete expansion is considerably higher than the efficiency of the ideal Otto engine. In practice the advantage of the complete-expansion engine is not so great. The cylinder must be larger for the same power and friction losses are thereby increased.

209. The Humphrey Gas Pump.—The principle of complete expansion is utilized in an ingenious manner in the Humphrey gas

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pump, a diagram of which is shown in Fig. 109. The pump has a gas cylinder *c* which is directly connected with the pressure tank *a* by a pipe *p*. The pipe passes through a suction tank *b* and is there provided with inlet valves *v*, *v*. The inlet valve *m* and exhaust valve *n* of the gas cylinder are fitted with an interlocking gear, so that when either valve closes it locks itself and releases the other valve. The cycle of operations is as follows.

1. The gas cylinder contains a compressed mixture of gas and air and the valves are closed. The mixture is ignited and

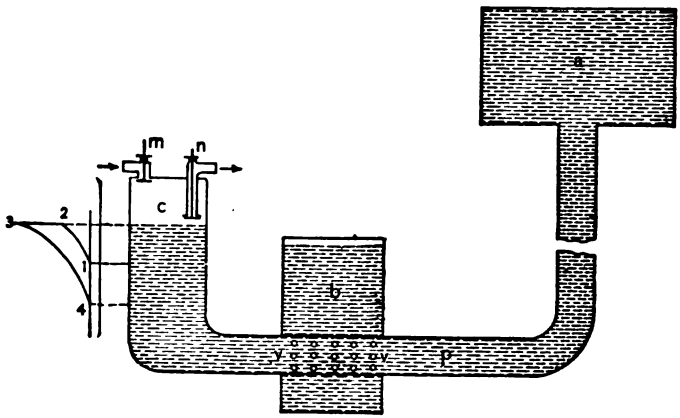


FIG. 109.

the pressure developed by the explosion drives the water from the gas cylinder and sets in motion the entire mass of water in the pipe *p*. The pressure of the expanding gases falls, as indicated by the curve 3–4 and the work of expansion is expended in raising the water. When the pressure of the expanding gases reaches atmospheric pressure the column of water is moving with considerable speed and continues in motion until its kinetic energy is used up. Consequently a partial vacuum is produced in the gas cylinder, the exhaust valve *n* opens, and water enters through the valves *v*,*v* and partially fills the gas cylinder, replacing the product of combustion.

2. The water column after coming to rest starts back and the water rising in the gas cylinder closes the exhaust valve by impact. The kinetic energy of the moving column is expended in com-

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pressing the remaining products of combustion in the cushion space of the gas cylinder.

3. After coming to rest the water column again moves towards the pressure tank actuated by the compressed gases in the cushion space. The pressure in the gas cylinder falls and when it reaches atmospheric pressure the inlet valve m opens and admits a fresh charge of fuel and air.

4. The oscillating water column returns the second time and compresses the charge as indicated by the curve 1–2. The compressed charge is ignited and the pressure rises as indicated by the combustion line 2–3.

It will be seen that the water column takes the place of the piston in the ordinary gas engine. The influx of water from the suction tank, in effect, increases the length of this piston so that the compression stroke 1–2 is shorter than the expansion stroke 3–4.

The theoretical efficiency of the gas pump, since it follows the complete expansion cycle, is greater than that of the gas engine operating on the Otto cycle. The tests that have been made indicate that the actual efficiency of the pump is somewhat greater than the efficiency of the gas engine with the same fuel and compression pressure.

EXERCISES

1. Work the example of Art. 202 taking the pressure at the end of compression (*a*) 90 lb., (*b*) 120 lb. per sq. in.; other data unchanged. Plot a curve showing the variation of the ideal efficiency with the compression pressure.

2. In the same example keep the compression pressure at 150 lb. but assume (*a*) 10 per cent., (*b*) 30 per cent. excess of air. Observe the variation of efficiency with the excess of air used.

3. In the example of Art. 203 take 39 lb. of air per pound of oil and find the efficiency.

4. A Diesel engine is to deliver 70 b.h.p. at 160 r.p.m. The mechanical efficiency is 0.80. With the results obtained in the example of Art. 203, calculate the volume displaced by the piston. Ans. 1.99 cu. ft.

5. Modify the solution of example 4 to take account of the following conditions. The actual cycle efficiency is reduced to 0.35 due to the loss of heat to the jacket, and the pressure at the beginning of compression is 13 lb. instead of 14.7 lb. Find the cylinder volume.

Ans. { 2.65 cu. ft.
{ 16 in. × 23 in.

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6. Calculate the ideal efficiency of an engine operating in the Otto cycle with each of the five gases whose compositions were given in the exercises of the preceding chapter. Assume $T_1 = 700$, $p_1 = 14.7$, and 20 per cent. excess of air, and take the following pressures at the end of compression. For No. 1, 180 lb.; for No. 2, 150 lb.; for No. 3, 80 lb.; for No. 4, 90 lb.; for No. 5, 120 lb.

7. Find the ratios of the calculated efficiencies to the air-standard efficiencies for the five cases.

8. For one of the problems in example 6 modify the solution to take account of the heat flowing to the jacket water. Assume that the heat rejected is 28 per cent. of the heat of combustion; 5 per cent. lost during combustion, 23 per cent. during expansion.

9. In the example of Art. 203 assume that 5 per cent. of the heat of combustion is lost during combustion and 25 per cent. during expansion. Calculate T_3, T_4, and n under these conditions.

10. Show that the efficiency of the Diesel cycle with complete expansion to the initial pressure is given by the expression

$$\eta = 1 - \frac{i_{p4} - i_{p1}}{\frac{M'}{M} H_p}.$$

REFERENCES

CLERK: The Gas, Petrol, and Oil Engine.
WIMPERIS: The Internal Combustion Engine.
CARPENTER and DIEDERICHS: Internal Combustion Engines.
LEVIN: Modern Gas Engine.
JONES: The Gas Engine.
Mechanical Engineers' Handbook, p. 1020–1037.

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CHAPTER XVII

MIXTURES OF GASES AND VAPORS

210. Moisture in the Atmosphere.—Because of evaporation of water from the earth's surface, atmospheric air always contains a certain amount of water vapor mixed with it. The weight of the vapor relative to the weight of the air is slight even when the vapor is saturated. Nevertheless, the moisture in air influences in a considerable degree the performance of air compressors, air refrigerating machines, and internal combustion motors; and in an accurate investigation of these machines the medium must be considered not dry air but rather a mixture of air and vapor. The study of air and vapor mixtures is also important in meteorology and especially in problems relating to heating and ventilation.

Experiment has shown that Dalton's law holds good within permissible limits for a mixture of gas and vapor. The gas has the pressure p' that it would have if the vapor were not present, and the vapor has the pressure p'' that it would have if the gas were not present. The pressure of the mixture is

$$p = p' + p''. \qquad (1)$$

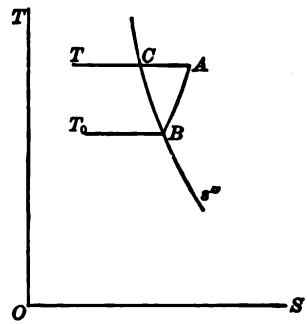


FIG. 110.

If the vapor is saturated, the temperature t of the mixture must be the saturation temperature corresponding to the pressure p''. If the temperature is higher than this, the vapor must be superheated.

The water vapor in the atmosphere is usually superheated. Let point A, Fig. 110, represent the state of the vapor, and let AB be a constant pressure curve cutting the saturation curve at B. Further, let m denote the weight per cubic foot of the vapor in the state A, and m_1, the weight per cubic foot of *satu-*

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rated vapor at the same temperature, that is, in the state C. The ratio $\frac{m}{m_1}$ is called the **humidity** of the air under the given conditions. If the mixture of air and vapor is cooled at constant pressure, the vapor will follow the path AB and at B it will become saturated. Upon further cooling some of the vapor will condense. The temperature T_0 at which condensation begins is called the **dew point** corresponding to the state A.

The humidity may be expressed approximately in terms of pressures. Let p_a'' denote the pressure of the vapor in the state A and p_c'' the pressure of saturated vapor at the same temperature, hence in the state represented by C. At the low pressures under consideration we may assume that the vapor follows the gas law $pV = MBT$. Hence, taking $V = 1$, we have

$$p_a'' = p_b'' = mBT,$$

and

$$p_c'' = m_1BT.$$

Therefore, denoting the humidity by ϕ, we have

$$\phi = \frac{m}{m_1} = \frac{p_b''}{p_c''}. \tag{2}$$

That is, the humidity is the ratio of the pressure corresponding to the dew point to the saturation pressure corresponding to the temperature of the mixture.

For investigations that involve hygrometric conditions, the data ordinarily required may be found in table 6 of the "Properties of Steam and Ammonia."

211. Heating or Cooling of Air.—In the case of dry air the calculation of the heat required to raise the temperature of a mass of air involves only the well known formula

$$Q = Mc(t_2 - t_1),$$

in which c is the specific heat for the conditions under which the heat is supplied. For constant pressure, the approximate value $c_p = 0.24$ has been used. In the 10th column of table 6 the values are based on Swann's expression for the specific heat of air, namely,

$$c_p = 0.24112 + 0.000009t.$$

The number opposite a given temperature gives the heat required

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to raise the temperature from 0° F. to that temperature. Thus for the range 0°–12° the heat required is 2.893 B. t. u., from 0° to 70° it is 16.90 B. t. u. Therefore to raise the temperature from 12° to 70° the heat required per pound of air is 16.90 − 2.89 = 14.01 B. t. u.

When water vapor is mixed with air, the calculation involves the properties of steam. In all cases of practical importance the heating or cooling proceeds at constant pressure, and the principle to be employed, therefore, is the following: *The heat absorbed (or rejected) is given by the difference between the thermal potentials at the initial and final states.* For the air, the difference in potential is obtained by subtracting the appropriate values in column 10 of table 6. The problem is reduced, therefore, to the determination of the change of thermal potential in the steam (or water) content.

The vapor in the air has a very low pressure and it is usually superheated; and for these conditions the ordinary table of properties of superheated steam cannot be used to advantage. However, the thermal potential is easily found. Since at low pressure superheated steam approaches the condition of a perfect gas, the thermal potential remains nearly constant when the temperature remains constant. This statement may be verified by the Mollier chart for steam. The potential of the vapor in the state represented by A, Fig. 110, is therefore practically equal to the potential of saturated steam at the same temperature; that is, $i_a = i_c$. For example the value of i'' for saturated steam at 85° F. is 1097.8 B. t. u. and this same number may be taken as the value of i for superheated steam at any lower pressure and at 85° F.

The following examples illustrate the application of the foregoing principles.

EXAMPLE 1. *Cooling.* Air at a temperature of 85° F. with 70 per cent. humidity is cooled to 70° F. Required the heat abstracted per pound of dry air.

If the air is saturated at 85° the weight of water vapor carried is, from table 6, 0.02634 lb.; hence for $\varphi = 0.70$, the water present is $0.02634 \times 0.70 = 0.01844$ lb. At 70° F. saturated air contains 0.01578 lb. per pound of dry air. In cooling from 85° to 70°, the weight 0.01844 − 0.01578 = 0.00266 lb. must be condensed.

At a temperature of 85° the thermal potential of 1 lb. of steam, saturated

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or superheated is 1097.8 B. t. u., and at 70° it is 1090.9 B. t. u. We have then the following schedule for the thermal potentials.

In the initial state		
1 lb. dry air at 85°	$i = 20.53$ B. t. u.	
0.01844 lb. vapor	$i = 0.01844 \times 1097.8 = 20.24$	
		40.77
In the final state		
1 lb. dry air at 70°	$i = 16.90$	
0.01578 lb. vapor	$i = 0.01578 \times 1090.9 = 17.21$	
0.00266 lb. water at 70°	$i = 0.00266 \times 38.1 = 0.10$	
		34.21

The heat abstracted per pound of dry air is therefore $i_1 - i_2 = 40.77 - 34.21 = 6.56$ B. t. u.; per pound of moist air in the initial condition, it is $6.56 \div 1.01844 = 6.44$ B. t. u.

EXAMPLE 2. Under the conditions of Ex. 1, required the capacity of a refrigerating machine to cool 15,000 cu. ft. of moist air per minute. From table 6 the volume of 1 lb. of dry air is 13.73 cu. ft., the volume of 1 lb. of dry air with 0.02634 lb. of water vapor is 14.31 cu. ft., and the volume of 1 lb. of dry air with 70 per cent. of this water vapor present is $13.73 + 0.7 \times 0.58 = 14.14$ cu. ft. Hence the volume of 1 lb. of the moist air in the initial condition is $14.14 \div 1.01844 = 13.88$ cu. ft. The weight of moist air entering the cooler per minute is $15{,}000 \div 13.88$, and the heat abstracted per minute is therefore $\frac{15{,}000}{13.88} \times 6.44 = 6960$ B. t. u. Since 1 ton of refrigeration is equivalent to 200 B. t. u. per min., the required capacity in tons is $6960 \div 200 = 34.8$.

EXAMPLE 3. *Humidifying Air.* A temperature of 70° F. with a humidity of 40 per cent. is to be maintained in a building. The outside air has a temperature of 0° F. and a humidity of 30 per cent. (*a*) Required the humidity in the building if the outside air is heated without the addition of water. (*b*) Find the water that must be added to give the desired humidity. (*c*) Find the heat required.

One pound of outside air has mixed with it $0.000781 \times 0.30 = 0.000234$ lb. of water vapor. At 70° one pound of air saturated carries 0.01578 lb. of water vapor. Hence if no water is added the humidity at 70° is $0.000234 \div 0.01578 = 0.015$, or 1.5 per cent.

With 40 per cent. humidity 1 lb. of air at 70° carries $0.40 \times 0.01578 = 0.00631$ lb. of water vapor, which is weight carried by 1 lb. of air at 45° when saturated. That is, 45° is the dew point corresponding to 40 per cent. humidity at 70° F. The outside air is first heated to 45°, it is then passed through a spray of water and thus becomes saturated, and then the mixture is heated to 70° F. The temperature of the water in the spray may be adjusted by a heater under the control of a thermostat; however, the water enters the heater at some definite initial temperature, which in

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this case we shall assume to be 60° F. The weight of water absorbed from the spray per pound of dry air is 0.00631 − 0.000234 = 0.006076 lb.

The thermal potential of superheated steam at 0° cannot be obtained from the tables; however, at this low temperature it does not differ greatly from the latent heat of vaporization. In column 11 of table 6, we find 0.964 as the latent heat in the water vapor contained in 1 lb. of dry air when saturated. With 30 per cent. humidity the latent heat of the steam present is 0.30 × 0.964 = 0.29 B. t. u., and this may be taken as the thermal potential. We have then the following:

In the initial state	
i of 1 lb. of air at 0° F.	= 0.0 B. t. u.
i of contained water vapor	= 0.29
i of 0.006076 lb. of water at 60° = 0.006076 × 28	= 0.17
	0.46 B. t. u.
In the final state	
i of 1 lb. dry air at 70°	= 16.90 B. t. u.
i of 0.00631 lb. vapor at 70° = 0.00631 × 1090.9	= 6.88
	23.78 B. t. u.

The heat required per pound of dry air is therefore

$$23.78 - 0.46 = 23.32 \text{ B. t. u.}$$

212. Theory of the Cooling Tower.—In the cooling tower warm water from the condensers comes in contact with a current of air at lower temperature and is thereby cooled to such a temperature that it may again be used in condenser. The cooling is effected in two ways: 1. The air absorbs the heat required to raise its temperature; 2. The vapor content of the air is increased as the temperature rises, and the water supplies the heat of vaporization.

Let M denote the weight of water cooled per pound of dry air circulated, and M_e the weight of water evaporated. If, then, i_1 and i_2 are, respectively, the thermal potentials per pound of water at the initial and final temperatures, the decrease of thermal potential is

$$Mi_1 - (M - M_e)i_2,$$

and this is the heat given up by the water. Let i_1' denote the potential of one pound of dry air and the vapor carried by it in the initial state, and i_2' the potential of one pound of the air leaving and the vapor mixed with it. The difference $i_2' - i_1'$ is the heat received by the air. Therefore we have

$$Mi_1 - (M - M_e)i_2 = i_2' - i_1', \qquad (1)$$

as the equation for the determination of the weight M.

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EXAMPLE. Water enters the cooling tower at 130° F. and is cooled to 78° F. The air enters at 68° F. with a humidity of 50 per cent. and leaves at 120° saturated with vapor. Required the volume of air needed to cool 22,000 lb. of water per hour.

One pound of dry air in the initial state carries $0.01471 \times 0.50 = 0.00735$ lb. of water vapor, and in the final state (saturated at 120°) it carries 0.0813 lb. Hence the difference $M_s = 0.0813 - 0.00735 = 0.074$ lb. is absorbed from the condensing water. The values of i_1 and i_2 are respectively 97.9 and 46.1 B. t. u. For the air in the initial state,

i of 1 lb. of dry air at 68° F. $= 16.42$ B. t. u.
i of 0.00735 lb. steam at 68° $= 0.00735 \times 1089.9 = 7.97$
$i_1' = 24.39$ B. t. u.

For the air in the final state,

i of 1 lb. of dry air at 120° $= 39.00$ B. t. u.
i of 0.0813 lb. of steam at 120° $= 0.0813 \times 1113.5 = 90.53$
$i_2' = 119.53$ B. t. u.

Substituting these values in (1),

$$97.9M - 46.1(M - 0.074) = 119.53 - 24.39,$$

or $$M = 1.77 \text{ lb.}$$

The weight of dry air required is

$$22{,}000 \div 1.77 = 12{,}430 \text{ lb.}$$

In the initial state the volume of the mixture of air and vapor per pound of dry air present is 13.45 cu. ft. Hence the volume of initial moist air required per hour is $12{,}430 \times 13.45 = 167{,}200$ cu. ft.

213. Mixture of Wet Steam and Air.—In a given volume V let there be M_1 lb. of air and M_2 lb. of saturated vapor mixture of quality x. The absolute temperature of the entire mixture is T, and the total pressure p, which is the sum of the partial pressures p' and p'' of the air and steam, respectively. We have, therefore

$$p' + p'' = p, \tag{1}$$
$$p'V = M_1BT, \tag{2}$$
$$V = M_2[x(v'' - v') + v'], \tag{3}$$

where, as usual, v'' and v' denote, respectively, the specific volumes of steam and water at the saturation temperature T.

The energy of the mixture is the sum of the energies of the two constituents; hence, we have

$$AU = M_1c_vT + M_2(i' + x\rho) + U_0. \tag{4}$$

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Likewise, the entropy of the mixture is

$$S = M_1\left[c_v \log_e T + AB \log_e \frac{V}{M_2}\right] + M_2\left(s' + \frac{xr}{T}\right) + S_0. \quad (5)$$

By means of these equations various changes of state may be investigated.

214. Isothermal Change of State.—Since T remains constant, we have from (4)

$$A(U_2 - U_1) = M_2 \rho (x_2 - x_1), \quad (1)$$

and from (5)

$$S_2 - S_1 = M_1 AB \log_e \frac{V_2}{V_1} + M_2 \frac{r}{T}(x_2 - x_1). \quad (2)$$

Hence, the heat added is given by the equation

$$Q = T(S_2 - S_1) = M_1 ABT \log_e \frac{V_2}{V_1} + M_2 r(x_2 - x_1). \quad (3)$$

The external work is

$$W = JQ - (U_2 - U_1) = M_1 BT \log_e \frac{V_2}{V_1} + JM_2(r - \rho)(x_2 - x_1)$$

$$= p_1' V_1 \log_e \frac{V_2}{V_1} + p_1''(V_2 - V_1). \quad (4)$$

The volume in the final state is

$$V_2 = M_2[x_2(v'' - v') + v'],$$

or neglecting the small water volume v',

$$V_2 = M_2 x_2 v'', \quad (5)$$

while the volume in the initial state is

$$V_1 = M_2 x_1 v''. \quad (6)$$

Hence, combining (5) and (6),

$$x_2 = \frac{V_2}{V_1} x_1. \quad (7)$$

From (7) it appears that isothermal expansion is accompanied by an increase of the quality x, that is, by evaporation, while isothermal compression involves condensation.

215. Adiabatic Change of State.—In the case of an adiabatic change the final total pressure p_2 is usually given. Assuming that the steam in the mixture does not become superheated, the final temperature T_2 of the mixture must be the saturation temperature corresponding to the partial pressure p_2'' of the steam. The determination of the final state of the mixture involves the determination of two unknown quantities; the par-

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tial pressure p_2'', and the quality x_2 of the saturated vapor. Hence two relations are required. One is given by the condition that the entropy of the mixture shall remain constant during the change, the other by the condition that the final volume V_2 may be considered as occupied by each constituent of the mixture independently of the other.

In the application of the first condition it is convenient to use an expression for the entropy of the mixture of a form different from that given by (5), Art. 213. In terms of the temperature and pressure, the entropy of a unit weight of air is given by the expression

$$s = c_p \log_e T - AB \log_e p + s_0;$$

hence for the mixture we have

$$S = M_1(c_p \log_e T - AB \log_e p') + M_2 \left(s' + \frac{xr}{T}\right) + S_0. \quad (1)$$

As the constant S_0 disappears when the difference of entropy between two states is taken, it may be ignored in the calculation.

Let S_1 denote the entropy in the initial state. Then since the entropy remains constant, we have

$$S_1 = M_1(c_p \log_e T_2 - AB \log_e p_2') + M_2 \left(s_2' + \frac{x_2 r_2}{T_2}\right). \quad (2)$$

In this equation S_1, M_1, M_2, and the coefficients c_p and AB are known, as is the final total pressure p_2. The partial pressures p_2' and p_2'', the quality x_2, and temperature T_2 are unknown. However, T_2 depends upon p_2'', and p_2' is found from the relation $p_2' + p_2'' = p_2$ when p_2'' is determined. Denoting the final volume by V_2, we have

$$V_2 = \frac{M_1 B T_2}{p_2'} = M_2 x_2 v_2'',$$

whence

$$x_2 = \frac{M_1 B T_2}{M_2 p_2' v_2''}. \quad (3)$$

Inserting this expression for x_2 in (2), we have finally

$$S_1 = M_1(c_p \log_e T_2 - AB \log_e p_2') + M_2 \left(s_2' + \frac{M_1}{M_2} \frac{B r_2}{p_2' v_2''}\right). \quad (4)$$

In this equation p_2' is the only unknown. The solution is most easily effected by assuming several values of p_2'' and calculating for these the values of the second member. These

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calculated values are then plotted as ordinates with the corresponding values of p_2'' as abscissas and the intersection of the curve thus obtained with the line S_1 = const. gives the desired value of p_2''.

Attention must be given to the units of pressure employed. In (3), and in the last term of (4), p_2' must be taken in pounds per square *foot*. In the term $AB \log_e p_2'$, however, the pressure may be taken in pounds per square inch, since the omitted term, $AB \log_e 144$, is a constant and may be included in the constant S_0.

The external work of expansion or compression is equal to the change of energy. Hence, using the general expression for the energy of the mixture, we have

$$AW = M_1 c_v (T_1 - T_2) + M_2(i'_1 - i'_2 + x_1\rho_1 - x_2\rho_2). \quad (5)$$

EXAMPLE. In a compressor cylinder suppose water to be injected at the beginning of compression in such a manner that the weight of water and water vapor is just equal to the weight of the air. Let the pressure of the mixture be normal atmospheric pressure 29.92 in. of mercury, and let the temperature be 79.1° F. The mixture is compressed to a pressure of 120 lb. per square inch absolute. Required the final state of the mixture and the work of compression per pound of air.

From the steam table the partial pressure of the water vapor corresponding to 79.1° is 1 in. Hg, hence the partial pressure of the air is 28.92 in. Hg. The initial quality x_1 is found from the relation

$$V_1 = \frac{M_1 B T_1}{p_1'} = M_2 x_1 v_1'',$$

whence $$x_1 = \frac{M_1 B T_1}{M_2 p_1' v_1''} = \frac{53.34 \times 538.7}{28.92 \times 0.4912 \times 144 \times 652} = 0.0215.$$

The factor 0.4912×144 is used to reduce pressure in inches of mercury to pounds per square foot.

For the entropy of the mixture we obtain from (1) (neglecting the constant S_0)

$$S_1 = 0.24 \log_e 538.7 - 0.0686 \log_e (28.92 \times 0.4912) + 0.0915 + 0.0215 \times 1.9455 = 1.4589.$$

Since the ratio of the final to the initial pressure of the mixture is $\frac{120}{14.7} =$ 8.2, we assume that the pressure p_2'' of the vapor after compression will be approximately 8 times the initial pressure p_1''. Hence we assume $p_2'' = 7$, 8, and 9 in. of mercury, respectively, and calculate the corresponding values of the second member of (4). Some of the details of the calculation are given.

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			From steam table					
p_2'' (in. Hg)	p_2'' lb./in.^{2}	p_2'	t_2	T_2	s_2'	r_2	v_2''	
7	3.43	116.57	146.9	606.5	0.2098	1010.5	104.4	
8	3.92	116.08	152.3	611.9	0.2187	1007.4	92.1	Data
9	4.41	115.59	157.1	616.7	0.2265	1004.6	82.5	

p_2''	$c_p \log_e T_2$	$AB \log_e p_2$	$\frac{Br_2}{p_2'v_2''}$	S	
7	1.5378	0.3264	0.0308	1.4519	
8	1.5400	0.3262	0.0349	1.4673	Results
9	1.5418	0.3259	0.0390	1.4814	

The pressure p_2'' that gives the value $S = 1.4589$ lies between 7 and 8 in. Hg and by the graphical method or by interpolation we find $p_2'' = 7.44$ in. Hg., or $p_2'' = 3.65$ lb. per square inch. Therefore $p_2' = 120 - 3.65 = 116.35$ lb. per square inch. From the steam table the following values are found for the pressure $p_2'' = 7.44$ in. Hg.: $t_2 = 149.3$, $T_2 = 608.9$, $i_2' = 117.2$, $r_2 = 1009.1$, $p_2 = 942.5$, $v_2'' = 99$. The final quality is

$$x_2 = \frac{BT_2}{p_2'v_2''} = \frac{53.34 \times 608.9}{116.35 \times 144 \times 99} = 0.01958.$$

The external work per pound of air is

$$W = J[0.17(149.3 - 79.1) + 117.2 - 47.1 + 0.0215 \times 988.7 - 0.01958 \times 942.5] = 65{,}970 \text{ ft. lb.}$$

The volume of the mixture at the end of compression is

$$V = \frac{BT_2}{p_2'} = \frac{53.34 \times 608.9}{116.35 \times 144} = 1.939 \text{ cu. ft.},$$

and the work of expulsion is therefore

$$1.939 \times 120 \times 144 = 33{,}500 \text{ ft. lb.}$$

Hence, the work of compression and expulsion is 99,740 ft. lb.

The effect of injecting water into a compressor cylinder may be shown by a comparison of the result just obtained with the work of compressing and expelling 1 lb. of dry air under the same conditions.

The initial volume of 1 lb. of air is $\frac{53.34 \times 538.7}{14.7 \times 144} = 13.574$ cu. ft.

The final volume after adiabatic compression to 120 lb. per square inch is

$$13.574\left(\frac{14.7}{120}\right)^{\frac{1}{1.4}} = 3.0296 \text{ cu. ft.}$$

The work of compression is

$$-\frac{1.44}{0.4}(14.7 \times 13.574 - 120 \times 3.0296) = 59{,}040 \text{ ft. lb.},$$

the work of expulsion is $3.0296 \times 120 \times 144 = 52{,}350$ ft. lb., and the sum is 111,390 ft. lb. The effect of water injection is therefore to reduce the volume and temperature at the end of compression and the work of compression and expulsion. The reduction of work is nearly 11 per cent.

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216. Mixture of Air with High-pressure Steam.—In the preceding articles, we have dealt with mixtures of steam and air in which the pressure of the vapor content was small. The suggestion has been made that a mixture of air at relatively high temperature and pressure and steam may be used as a medium for heat engines. An analysis of the action of such a medium in a motor requires in the first place a discussion of the process of mixing, afterwards a discussion of the change of state of the mixture.

As carried out in an actual installation, the process of mixing would be somewhat as follows: Steam at an initial pressure p_1'' flows from the boiler to the engine through a main a, Fig. 111.

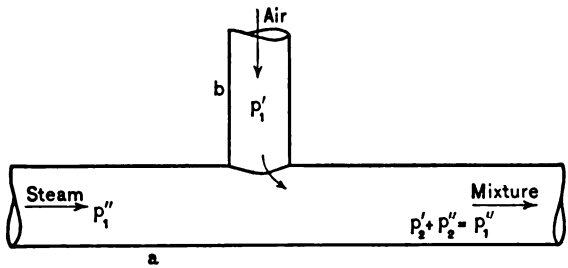


FIG. 111.

Compressed air at a pressure p_1', somewhat higher than p_1'', enters the main through a pipe b. The steam and air mix and the mixture has the initial pressure p_1'' of the steam. The partial pressures of air and steam in the mixture are, respectively, p_2' and p_2'', and the sum of these is p_1''.

To determine the state of the components in the mixture, that is, the partial pressures p_2', p_2'', the common temperature t_2, and the volume, two equations of condition must be established. One of these conditions is given by the fact that the volume of the mixture is at the same time the volume of the air at the pressure p_2' and the temperature t_2 and the volume of the steam at pressure p_2'' and the same temperature. The second equation may be derived by the application of the energy equation to the process.

Let V denote the volume of the mixture, V_1'' the volume of steam before mixing, and V_1' the volume of the air before mixing. Also let U_1' and U_2' denote, respectively, the energy of the air before and after mixing; and U_1'' and U_2'', respectively, the energy

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of the steam before and after mixing. In the main there is an increase of volume $(V - V_1'')$ and the work done against the pressure p_1'' is the product $p_1''(V - V_1'')$. The work done on the air in forcing it into the main is the product $p_1'V_1'$. Therefore the net work done by the system during the mixing process is $p_1''(V - V_1'') - p_1'V_1'$. Assuming that the process is adiabatic this work is equal to the decrease of energy; hence

$$U_1' + U_1'' - (U_2' + U_2'') = p_1''(V - V_1'') - p_1'V_1',$$

or
$$U_1' + p_1'V_1' + U_1'' + p_1''V_1'' = U_2' + U_2'' + p_1''V. \quad (1)$$

The sum $U + pV$ is the thermal potential I; in the second member of (1) the sum $U_2' + U_2''$ is the energy of the mixture, and $p_1''V$ is the product of the pressure and volume of the mixture. Hence (1) may be written

$$I_{\text{air}} + I_{\text{steam}} = I_{\text{mixture}}. \quad (2)$$

That is, the thermal potential of the mixture is the sum of the thermal potentials of the components before mixing.

EXAMPLE. Steam is supplied from the boiler at a pressure of 150 lb. per sq. in. and a quality 0.98; and the air is compressed to a pressure of 180 lb. per sq. in. and a temperature of 600° F. The mixing ratio is 1 lb. of air to 2 lb. of steam, or 0.5 lb. of air to 1 lb. of steam.

It is evident that the temperature t_2 of the mixture will be lower than 600°, and that the heat given up by the air will evaporate the water present and probably superheat the steam. The initial potential of 1 lb. of steam is 1177.4 B. t. u. The decrease in the potential of the air is $0.5 \times 0.24(600 - t_2)$; hence the potential of the steam in the mixture must be

$$i_2 = 1177.4 + 0.12(600 - t_2) = 1249.4 - 0.12\,t_2. \quad (a)$$

At the final pressure p_2' and temperature t_2 the volume of 0.5 lb. of air is given by the equation

$$144p_2'V = 0.5BT_2$$

or

$$V = \frac{B}{288}\frac{T_2}{p_2'}. \quad (b)$$

We choose now a tentative value of t_2, determine i_2 of the superheated steam from (a) and then from the table of superheated steam, find the pressure p_2'' corresponding to these values of t_2 and i_2. We observe also the corresponding volume v of 1 lb. of superheated steam. Subtracting p_2'' from p_1'', we obtain the partial pressure p_2' of the air, and substitute in (b). If the volume obtained from (b) agrees with that observed in the table the assumed value of t_2 is correct.

In this case, a preliminary trial shows that t_2 lies between 360° and 370°. We take the three temperatures 360, 365, 370 and arrange the computation according to the following schedule.

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t_2 =	360.0	365.0	370.0
$0.12t_2$ =	43.2	43.8	44.4
$1249.4 - 0.12t_2$ =	1206.2	1205.6	1205.0
p_2'' (from table) =	100.5	117.0	134.0 lb.
v (from table) =	4.65	3.98	3.48
$p_2' = 150 - p_2''$	49.5	33.0	16.0
T_2 =	819.6	824.6	829.6
$\log T_2$ =	2.91360	2.91624	2.91887
$\log \frac{B}{288}$ =	$\bar{1}.26766$	$\bar{1}.26766$	$\bar{5}.26766$
	2.18126	2.18390	2.18653
$\log p_2'$ =	1.69461	1.51851	1.20412
$\log v$ =	0.48665	0.66539	0.98241
v =	3.07	4.63	9.61

The curves for the two sets of values of v intersect at $t_2 = 363.8$, the corresponding value of i_2 is 1205.7, and the pressure of the steam is found to be $p_2'' = 113$ lb. Hence the partial pressure of the air is 37 lb.

217. Comparison of Efficiencies.—The ideal cycle of an engine using as a medium a mixture of steam and air is similar to the Rankine cycle of an engine using steam alone. The mixture expands adiabatically to the back pressure p_2 and is then expelled from the cylinder at that pressure. Obviously the injection of air into steam is practicable in non-condensing engines only; hence the pressure p_2 must be equal to or greater than the pressure of the atmosphere.

As in the Rankine cycle, the work delivered per cycle is equal to the decrease of thermal potential during adiabatic expansion. Denoting by the subscripts 2 and 3, respectively, the state of the mixture at the beginning and end of adiabatic expansion, the decrease in the thermal potential of the steam is $M_2(i_2 - i_3)$ and that of the air is $M_1c_p(t_2 - t_3)$: hence

$$A(W) = M_2(i_2 - i_3) + M_1c_p(t_2 - t_3). \qquad (1)$$

Part of this work, however, must be used to compress the air injected into the steam. If t_a is the initial temperature of the air and t_1 the final temperature after adiabatic compression, the work required for compression (see Art. 158) is

$$AW_c = M_1c_p(t_1 - t_a). \qquad (2)$$

The net work delivered per pound of steam is therefore

$$AW = i_2 - i_3 + \frac{M_1}{M_2}c_p(t_2 - t_3) - \frac{M_1}{M_2}c_p(t_1 - t_a). \qquad (3)$$

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To investigate the effect of air injection on the efficiency of the engine, let us take two non-condensing engines each taking steam at a pressure of 150 lb. and quality 0.98 and expanding to a back pressure of 16 lb. per sq. in. One uses steam alone, the other steam mixed with air under the condition stated in the preceding example. For the same power the engines will have different cylinder volumes and different expansion ratios. It is assumed that each engine follows the ideal Rankine cycle.

(*a*) *Engine Using Air-steam Mixture.*—From the preceding example the state of the mixture at the beginning of adiabatic expansion is as follows: p_2'' (of steam) = 113 lb.; p_2' (of air) = 37 lb.; $t_2 = 363.8°$; $T_2 = 823.4$. From the steam table the entropy of 1 lb. of steam in this state is 1.6130. The entropy of 0.5 lb. of air in the given state is

$$0.5(0.24 \log_e 823.4 - 0.0686 \log_e 37) = 0.6818$$

The entropy of the mixture is therefore 1.6130 + 0.6818 = 2.2948, and this is also the entropy in the final state at 16 lb. pressure. We have now to adjust the partial pressures p_3' and p_3'' at the end of expansion so that the sum $p_3' + p_3'' = 16$ lb. and the entropy of the mixture is 2.2948. We assume therefore probable values of the partial steam pressure p_3'', calculate values of x_3 from the relation $x_3 = \frac{M_1}{M_2}\frac{BT_3}{p_3 v_3''}$, and then values of the entropy of the steam. The details of the calculation are as follows:

p_3'' (assumed)	10	11	12 lb.
$p_3' = 16 - p_3''$	6	5	4
From table t_3	193.2	197.8	202.0
From table T_3	652.8	657.4	661.6
From table v_3''	38.43	35.16	32.41
From table $\frac{r_3}{T_3}$	1.5062	1.4916	1.4783
$\log T_3$	2.81478	2.81783	2.82060
$\log \frac{0.5B}{144}$	$\bar{1}.26766$	$\bar{1}.26766$	$\bar{1}.26766$
	2.08244	2.08559	2.08826
$\log p_3'$	0.77815	0.69897	0.60206
$\log v_3''$	1.58467	1.54605	1.51068
$\log x_3 = \log \frac{0.5BT_3}{p_3' v_3''}$	$\bar{1}.71962$	$\bar{1}.84057$	$\bar{1}.97552$
$\log \frac{r_3}{T_3}$	0.17788	0.17365	0.16976
	$\bar{1}.89750$	0.01422	0.14528
$x_3 \frac{r_3}{T_3}$	0.7898	1.0333	1.3972
s_3'	0.2835	0.2905	0.2969
Entropy of steam	1.0733	1.3238	1.6941

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For the entropy of the air we have the following schedule:

p_3'	6	5	4	
T_3	652.8	657.4	661.6	
$\log_e T_3$	6.48127	6.48829	6.49466	
$0.24 \log_e T_3$	1.55551	1.55719	1.55872	(a)
$\log_e p_3'$	1.79176	1.60944	1.38629	
$0.0686 \log_e p_3'$	0.12290	0.11041	0.09510	(b)
$(a) - (b)$	1.4336	1.4468	1.4636	
$0.5[(a) - (b)]$	0.7168	0.7234	0.7318	

These are the values of the entropy of 0.5 lb. of air in the state 3. Adding these to the values found for the steam, we have

S_3 of mixture	1.7901	2.0472	2.4259

Plotting these values, we find that the curve intersects the line $S_3 = 2.2948$ at the point $p_3'' = 11.7$ lb. per sq. in. From the steam table we have $t_3 = 200.7$, $r_3 = 978.8$, $i_3' = 168.6$, $v_3'' = 33.43$. Also $p_3' = 4.3$ lb. For the quality x_3 we have $x_3 = \frac{0.5BT_3}{144p_3'v_3''} = 0.872$; hence the final potential of the steam is $i_3' + x_3r_3 = 168.6 + 0.872 \times 978.8 = 1001.2$ B. t. u. In the initial state the thermal potential was 1205.7 B. t. u. The work of the cycle for 1 lb. of steam is therefore

$A(W) = 1205.7 - 1001.2 + 0.5 \times 0.24(363.8 - 200.7) = 224.1$ B. t. u.

The air is compressed adiabatically from 14.7 lb. to 180° lb. and the temperature range is from $t_a = 78°$ to $t_1 = 600°$. The work of compression is,

$$AW_c = Mc_p(t_1 - t_a) = 0.5 \times 0.24(600 - 78) = 62.6 \text{ B. t. u.}$$

Hence the net work per pound of steam is $224.1 - 62.6 = 161.5$ B. t. u.

(*b*) *Engine Using Steam.*—The thermal potential at the beginning of adiabatic expansion is $1194.7 - 0.02 \times 864.9 = 1177.4$ B. t. u. and the entropy is $1.5704 - 0.02 \times 1.0573 = 1.5493$. The quality after adiabatic expansion to 16 lb. is found from the equation $1.5493 = s_3' + x_3 \frac{r_3}{T_3} = 0.3184 + 1.4337x_3$; from which $x_3 = 0.859$. The thermal potential is $i_3 + x_3r_3 = 184.3 + 0.859 \times 969.1 = 1016.3$ B. t. u. The work per pound of steam is, therefore, $1177.4 - 1016.3 = 161.1$ B. t. u.

It appears from these results that the increase of the ideal efficiency obtained by the injection of air is insignificant. Better results might be shown with a larger ratio of air to steam. The practical advantage of air injection is not the improvement of the ideal efficiency but rather an improvement of the potential efficiency. Since the entering medium is a mixture of air and superheated steam, the loss due to initial condensation on the cylinder head and walls must be somewhat reduced.

Whether the possible increase of efficiency obtained by air injection can be made to justify the added expense of the com-

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pressor and the larger cylinder volume required is a question that has not been definitely answered.

EXERCISES

1. The temperature of air is 85° and the dew point is 70° F. Find the humidity and the weight of water vapor per pound of dry air.

Ans. $\begin{cases} 0.599 \\ 0.01578 \text{ lb.} \end{cases}$

2. The humidity is 0.60 when the atmospheric temperature is 74° F. Find the dew point. Ans. 59.5° F.

3. Air at 90° F. with 70 per cent. humidity is cooled to 42°. How much water is condensed per pound of dry air? If the saturated air at 42° is heated to 70° what will be the humidity?

Ans. $\begin{cases} 0.01614 \text{ lb.} \\ 0.357 \end{cases}$

4. Find the heat that must be abstracted per pound of dry air in cooling the air from the initial state to 42°. Ans. 29.34 B. t. u.

5. Water enters a cooling tower at 115° F. and is cooled to 80°. Air enters at 70° with 65 per cent. humidity and leaves at 110° saturated with vapor. Find the volume of air required per pound of water cooled.

Ans. 7.68 cu. ft.

6. A mixture of air and wet steam has a volume of 3 cu. ft. and the temperature is 240° F. The weight of the air present is 1 lb., that of the steam and water 0.4 lb. Find the partial pressures of the air and vapor, the total pressure of the mixture, and the quality of the steam.

Ans. $\begin{cases} p' = 86.38 \text{ lb.} \\ x = 0.459 \end{cases}$

7. The mixture in Ex. 6 expands isothermally to a volume of 5 cu. ft. Find the external work, the heat added, the change of entropy, and the change of energy. Ans. ${}_1W_2 = 26{,}254$ ft. lb.

8. The mixture expands adiabatically to a volume of 5 cu. ft. Find the condition of the mixture after expansion, and the external work.

Ans. $\begin{cases} t_2 = 206.2°; x_2 = 0.418 \\ {}_1W_2 = 23{,}130 \text{ ft.-lb.} \end{cases}$

9. In the example of Art. 217 use 1 lb. of air per pound of steam, leaving the remaining data unchanged. Find the condition of the mixture after the mixing process is completed.

Ans. $\begin{cases} p'' = 91 \text{ lb.}; p' = 59 \text{ lb.} \\ t = 394.8° \end{cases}$

10. Find the state of the mixture after adiabatic expansion to a pressure of 16 lb. per sq. in.

Ans. $\begin{cases} p'' = 9.24 \text{ lb.}; p' = 6.76 \text{ lb.} \\ t = 189.5°, \quad x = 0.86 \end{cases}$

11. Find the net heat transformed into work per pound of steam under the conditions of Ex. 10 and 11. Ans. 166.2 B. t. u.

12. Find the ratio of the cylinder volumes of the two engines referred to in Art. 217.

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TABLE I

Properties of Saturated Steam

Pressure Inches of Hg.	Temp. Fahr.	Heat Content		Latent Heat		Entropy			Volume of one Pound
		of Liquid	of Vapor	Total	Internal	of Liquid	of Vaporisation	of Vapor	
p	t	i'	i''	r	ρ	s'	$\frac{r}{T}$	s''	v
0.5	58.81	26.9	1087.1	1060.2	1002.9	.0532	2.0431	2.0963	1259.3
1.0	79.12	47.2	1096.7	1049.5	989.8	.0916	1.9482	2.0398	656.7
1.5	91.90	59.9	1102.5	1042.6	982.2	.1150	1.8905	2.0055	443.0
2.0	101.27	69.2	1106.6	1037.4	975.9	.1317	1.8497	1.9814	338.3
2.5	108.81	76.7	1109.9	1033.2	970.8	.1451	1.8178	1.9629	274.3
3.0	115.15	83.1	1112.7	1029.6	966.5	.1561	1.7915	1.9476	231.2
3.5	120.63	88.5	1115.0	1026.5	962.8	.1656	1.7692	1.9348	200.1
4.0	125.48	93.4	1117.1	1023.7	959.5	.1739	1.7497	1.9236	176.6
4.5	129.85	97.7	1118.9	1021.2	956.5	.1813	1.7325	1.9138	158.1
5.0	133.81	101.7	1120.6	1018.9	953.7	.1880	1.7170	1.9050	143.2
6	140.83	108.7	1123.4	1014.7	948.8	.1997	1.6901	1.8898	120.7
7	146.90	114.8	1125.9	1011.1	944.7	.2097	1.6672	1.8769	104.4
8	152.28	120.2	1128.0	1007.9	940.9	.2186	1.6473	1.8659	92.2
9	157.12	125.0	1130.0	1005.0	937.5	.2265	1.6296	1.8561	82.6
10	161.52	129.4	1131.7	1002.3	934.3	.2336	1.6138	1.8474	74.8
11	165.57	133.4	1133.3	999.9	931.5	.2401	1.5994	1.8395	68.38
12	169.31	137.2	1134.7	997.6	928.8	.2460	1.5862	1.8322	63.03
13	172.80	140.6	1136.0	995.4	926.3	.2516	1.5739	1.8254	58.48
14	176.07	143.9	1137.3	993.4	924.0	.2568	1.5627	1.8195	54.55
15	179.16	147.0	1138.5	991.5	921.8	.2616	1.5522	1.8138	51.13
16	182.08	150.0	1139.6	989.6	919.6	.2662	1.5423	1.8085	48.11
17	184.84	152.7	1140.6	987.9	917.6	.2705	1.5330	1.8035	45.46
18	187.47	155.4	1141.6	986.2	915.7	.2746	1.5242	1.7988	43.09
19	189.99	157.9	1142.5	984.6	913.8	.2785	1.5158	1.7943	40.96
20	192.38	160.3	1143.4	983.1	912.1	.2822	1.5079	1.7901	39.04
21	194.69	162.6	1144.2	981.6	910.4	.2857	1.5003	1.7860	37.29
22	196.91	164.8	1145.0	980.2	908.8	.2891	1.4931	1.7822	35.68
23	199.04	167.0	1145.8	978.8	907.2	.2923	1.4862	1.7785	34.22
24	201.10	169.0	1146.5	977.5	905.7	.2955	1.4796	1.7751	32.88
25	203.09	171.0	1147.2	976.2	904.2	.2985	1.4732	1.7717	31.65
26	205.01	173.0	1147.9	974.9	902.7	.3014	1.4670	1.7674	30.52
27	206.87	174.9	1148.6	973.7	901.4	.3042	1.4611	1.7653	29.46
28	208.68	176.7	1149.2	972.5	900.0	.3069	1.4554	1.7623	28.47
29	210.43	178.4	1149.8	971.4	898.8	.3095	1.4499	1.7594	27.55

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Pressure Lb. per Sq. In.	Temp. Fahr.	Heat Content		Latent Heat		Entropy			Volume of One Pound
		of Liquid	of Vapor	Total	Internal	of Liquid	Vaporization	of Vapor	
p	t	i'	i''	r	ρ	s'	$\frac{r}{T}$	s''	v''
14.7	212.0	180.0	1150.4	970.4	897.7	.3121	1.4449	1.7570	26.73
15	213.0	181.1	1150.8	969.7	896.8	.3137	1.4417	1.7554	26.23
16	216.3	184.4	1152.0	967.6	894.5	.3186	1.4315	1.7501	24.68
17	219.4	187.5	1153.0	965.5	892.1	.3231	1.4220	1.7451	23.32
18	222.4	190.5	1154.1	963.6	889.9	.3275	1.4129	1.7404	22.10
19	225.2	193.4	1155.0	961.6	887.7	.3317	1.4043	1.7360	21.00
20	227.9	196.1	1155.9	959.8	885.7	.3357	1.3961	1.7318	20.01
21	230.5	198.7	1156.8	958.1	883.8	.3395	1.3883	1.7278	19.12
22	233.0	201.2	1157.7	956.5	882.0	.3431	1.3809	1.7240	18.31
23	235.4	203.6	1158.5	954.8	880.0	.3467	1.3738	1.7205	17.57
24	237.8	206.0	1159.2	953.2	878.0	.3501	1.3669	1.7170	16.89
25	240.0	208.3	1160.0	951.7	876.2	.3533	1.3604	1.7137	16.27
26	242.2	210.5	1160.7	950.2	874.5	.3565	1.3540	1.7105	15.70
27	244.3	212.7	1161.5	948.8	872.9	.3595	1.3479	1.7074	15.17
28	246.4	214.8	1162.1	947.3	871.2	.3625	1.3419	1.7044	14.70
29	248.4	216.8	1162.8	946.0	869.8	.3653	1.3362	1.7015	14.21
30	250.3	218.8	1163.4	944.6	868.2	.3681	1.3307	1.6988	13.76
31	252.2	220.7	1164.0	943.3	866.8	.3708	1.3253	1.6961	13.34
32	254.0	222.5	1164.6	942.1	865.4	.3734	1.3201	1.6935	12.94
33	255.8	224.3	1165.1	940.8	864.0	.3760	1.3151	1.6911	12.57
34	257.6	226.1	1165.7	939.6	862.7	.3784	1.3102	1.6886	12.22
35	259.3	227.8	1166.2	938.4	861.3	.3808	1.3054	1.6863	11.89
36	261.0	229.5	1166.8	937.3	860.1	.3832	1.3008	1.6840	11.58
37	262.6	231.2	1167.3	936.1	858.8	.3855	1.2963	1.6818	11.29
38	264.2	232.8	1167.8	935.0	857.6	.3878	1.2918	1.6796	11.02
39	265.7	234.4	1168.3	933.9	856.4	.3900	1.2876	1.6776	10.76
40	267.3	236.0	1168.8	932.8	855.1	.3921	1.2834	1.6755	10.50
41	268.8	237.5	1169.3	931.8	854.0	.3942	1.2793	1.6735	10.26
42	270.2	239.0	1169.7	930.7	852.8	.3962	1.2753	1.6715	10.03
43	271.7	240.5	1170.1	929.7	851.7	.3982	1.2714	1.6696	9.81
44	273.1	241.9	1170.6	928.7	850.6	.4002	1.2676	1.6678	9.60
45	274.5	243.3	1171.0	927.7	849.5	.4021	1.2638	1.6659	9.40
46	275.8	244.6	1171.4	926.8	848.5	.4040	1.2602	1.6642	9.21
47	277.2	246.0	1171.8	925.8	847.4	.4059	1.2566	1.6625	9.02
48	278.5	247.3	1172.2	924.9	846.4	.4077	1.2531	1.6608	8.85
49	279.8	248.7	1172.6	923.9	845.3	.4095	1.2496	1.6591	8.68
50	281.1	250.0	1173.0	923.0	844.4	.4112	1.2463	1.6575	8.51
51	282.3	251.3	1173.4	922.1	843.4	.4130	1.2429	1.6559	8.36
52	283.5	252.6	1173.8	921.2	842.4	.4147	1.2397	1.6544	8.20
53	284.8	253.8	1174.2	920.4	841.5	.4164	1.2365	1.6529	8.06
54	286.0	255.0	1174.5	919.5	840.5	.4180	1.2333	1.6513	7.92
55	287.1	256.2	1174.9	918.7	839.6	.4196	1.2303	1.6499	7.78
56	288.3	257.4	1175.2	917.8	838.7	.4212	1.2272	1.6484	7.65
57	289.4	258.6	1175.6	917.0	837.8	.4228	1.2243	1.6471	7.52
58	290.6	259.7	1175.9	916.2	836.9	.4243	1.2213	1.6456	7.40
59	291.7	260.8	1176.2	915.4	836.0	.4258	1.2184	1.6442	7.28

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Pressure Lb. per Sq. In.	Temp. Fahr.	Heat Content		Latent Heat		Entropy			Volume of One Pound
		of Liquid	of Vapor	Total	Internal	of Liquid	Vaporization	of Vapor	
p	t	i'	i''	r	ρ	s'	$\frac{r}{T}$	s''	v''
60	292.8	262.0	1176.6	914.6	835.2	.4273	1.2156	1.6429	7.168
61	293.9	263.1	1176.9	913.8	834.3	.4288	1.2128	1.6416	7.057
62	294.9	264.2	1177.2	913.0	833.4	.4302	1.2101	1.6403	6.949
63	296.0	265.3	1177.5	912.2	832.5	.4316	1.2074	1.6390	6.845
64	297.0	266.3	1177.8	911.5	831.8	.4330	1.2047	1.6378	6.744
65	298.0	267.4	1178.1	910.7	830.9	.4344	1.2021	1.6365	6.646
66	299.1	268.4	1178.4	910.0	830.2	.4358	1.1995	1.6353	6.551
67	300.1	269.5	1178.7	909.2	829.3	.4372	1.1969	1.6341	6.459
68	301.1	270.5	1179.0	908.5	828.5	.4385	1.1944	1.6329	6.370
69	302.0	271.5	1179.3	907.8	827.7	.4398	1.1920	1.6318	6.283
70	303.0	272.4	1179.5	907.1	827.0	.4411	1.1895	1.6306	6.198
71	303.9	273.4	1179.8	906.4	826.2	.4424	1.1871	1.6295	6.115
72	304.9	274.4	1180.1	905.7	825.5	.4437	1.1847	1.6284	6.035
73	305.8	275.4	1180.4	905.0	824.7	.4450	1.1823	1.6273	5.957
74	306.8	276.3	1180.6	904.3	823.9	.4462	1.1800	1.6262	5.882
75	307.7	277.3	1180.9	903.6	823.2	.4474	1.1777	1.6251	5.809
76	308.6	278.2	1181.1	902.9	822.4	.4486	1.1755	1.6241	5.737
77	309.5	279.1	1181.4	902.3	821.8	.4498	1.1732	1.6230	5.666
78	310.4	280.0	1181.6	901.6	821.0	.4510	1.1710	1.6220	5.597
79	311.2	280.9	1181.9	901.0	820.4	.4522	1.1688	1.6210	5.530
80	312.1	281.8	1182.1	900.3	819.6	.4533	1.1667	1.6200	5.464
82	313.8	283.6	1182.7	899.0	818.2	.4556	1.1625	1.6181	5.338
84	315.5	285.3	1183.1	897.8	816.9	.4578	1.1584	1.6162	5.219
86	317.2	287.0	1183.6	896.6	815.6	.4600	1.1543	1.6143	5.104
88	318.8	288.7	1184.0	895.4	814.3	.4622	1.1503	1.6125	4.995
90	320.4	290.3	1184.5	894.2	813.0	.4642	1.1465	1.6107	4.890
92	321.9	291.9	1184.9	893.0	811.7	.4663	1.1427	1.6090	4.789
94	323.4	293.5	1185.3	891.8	810.4	.4683	1.1390	1.6073	4.692
96	324.9	295.0	1185.7	890.7	809.3	.4703	1.1353	1.6056	4.599
98	326.5	296.6	1186.1	889.5	808.0	.4723	1.1317	1.6040	4.511
100	327.9	298.1	1186.5	888.4	806.8	.4742	1.1282	1.6024	4.425
102	329.3	299.6	1186.9	887.3	805.6	.4761	1.1248	1.6009	4.343
104	330.7	301.0	1187.3	886.3	804.6	.4779	1.1214	1.5993	4.264
106	332.1	302.5	1187.7	885.2	803.4	.4797	1.1181	1.5978	4.188
108	333.5	303.9	1188.1	884.2	802.3	.4815	1.1149	1.5964	4.114
110	334.8	305.3	1188.4	883.1	801.1	.4833	1.1117	1.5950	4.043
112	336.2	306.7	1188.8	882.1	800.0	.4850	1.1085	1.5935	3.975
114	337.5	308.0	1189.1	881.1	799.0	.4867	1.1054	1.5921	3.909
116	338.8	309.4	1189.5	880.1	797.9	.4884	1.1024	1.5908	3.845
118	340.1	310.7	1189.8	879.1	796.8	.4901	1.0994	1.5895	3.784
120	341.3	312.0	1190.1	878.2	795.8	.4917	1.0965	1.5882	3.724
122	342.6	313.3	1190.5	877.2	794.8	.4933	1.0936	1.5869	3.666
124	343.8	314.5	1190.8	876.3	793.8	.4949	1.0907	1.5856	3.610
126	345.0	315.8	1191.1	875.3	792.7	.4965	1.0879	1.5844	3.555
128	346.2	317.0	1191.4	874.4	791.8	.4980	1.0851	1.5831	3.502

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Pressure Lb. per Sq. In.	Temp. Fahr.	Heat Content		Latent Heat		Entropy			Volume of One Pound
		of Liquid	of Vapor	Total	Internal	of Liquid	Vaporisation	of Vapor	
p	t	i'	i''	r	ρ	s'	$\frac{r}{T}$	s''	v''
130	347.4	318.2	1191.7	873.5	790.8	.4995	1.0824	1.5819	3.452
132	348.6	319.4	1192.0	872.6	789.9	.5010	1.0797	1.5807	3.402
134	349.7	320.6	1192.3	871.7	788.9	.5025	1.0770	1.5795	3.354
136	350.8	321.8	1192.6	870.8	788.0	.5039	1.0744	1.5783	3.307
138	352.0	323.0	1192.9	869.9	787.0	.5054	1.0719	1.5773	3.262
140	353.1	324.2	1193.2	869.0	786.1	.5068	1.0693	1.5761	3.218
142	354.2	325.3	1193.5	868.2	785.2	.5082	1.0668	1.5750	3.175
144	355.3	326.5	1193.8	867.3	784.3	.5096	1.0644	1.5740	3.133
146	356.4	327.6	1194.0	866.5	783.4	.5110	1.0619	1.5729	3.092
148	357.4	328.7	1194.3	865.6	782.4	.5123	1.0595	1.5718	3.052
150	358.5	329.8	1194.6	864.8	781.6	.5137	1.0571	1.5708	3.014
160	363.6	335.0	1195.8	860.8	777.4	.5202	1.0456	1.5658	2.834
170	368.5	340.2	1197.1	856.9	773.2	.5263	1.0349	1.5612	2.676
180	373.1	345.0	1198.2	853.2	769.3	.5321	1.0246	1.5567	2.534
190	377.6	349.6	1199.3	849.6	765.5	.5377	1.0149	1.5526	2.407
200	381.8	354.1	1200.3	846.2	762.0	.5430	1.0057	1.5487	2.292
210	385.9	358.4	1201.3	842.9	758.5	.5481	.9968	1.5449	2.188
220	389.9	362.5	1202.2	839.6	755.1	.5530	.9884	1.5414	2.093
230	393.7	366.5	1203.0	836.5	751.8	.5577	.9803	1.5380	2.006
240	397.4	370.4	1203.9	833.5	748.7	.5622	.9726	1.5348	1.926
250	401.0	374.1	1204.7	830.6	745.7	.5666	.9651	1.5317	1.852
260	404.5	377.8	1205.5	827.7	742.7	.5708	.9579	1.5287	1.784
270	407.8	381.3	1206.2	824.9	739.8	.5749	.9510	1.5259	1.722
280	411.1	384.7	1206.9	822.2	737.0	.5788	.9443	1.5231	1.663
290	414.3	388.1	1207.6	819.5	734.2	.5826	.9378	1.5204	1.608
300	417.4	391.3	1208.3	817.0	731.5	.5863	.9315	1.5178	1.558

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TABLE II

Properties of Saturated Steam below 212° F.

Temp. Fahr.	Pressure		Volume of One Pound (Cu. Ft.)	Weight of One Cubic Foot		Total Heat	Latent Heat	Temp. Fahr.
	Lb. per Sq. In.	Inches of Hg.		Pounds	Grains			
t	p	—	v''	γ	—	q''	r	t
32	0.0885	0.1802	3288	0.000304	2.129	1073.7	1073.7	32
34	0.0960	0.1955	3047	0.000328	2.297	1074.7	1072.7	34
36	0.1039	0.2116	2826	0.000354	2.477	1075.8	1071.7	36
38	0.1125	0.2291	2623	0.000381	2.669	1076.8	1070.8	38
40	0.1217	0.2478	2437	0.000410	2.872	1077.8	1069.8	40
42	0.1315	0.2677	2265	0.000442	3.091	1078.8	1068.8	42
44	0.1420	0.2891	2107	0.000475	3.322	1079.8	1067.7	44
46	0.1532	0.3119	1961	0.000510	3.570	1080.8	1066.7	46
48	0.1653	0.3366	1827	0.000547	3.831	1081.8	1065.7	48
50	0.1781	0.3627	1703	0.000587	4.110	1082.8	1064.7	50
52	0.1918	0.3905	1587	0.000630	4.411	1083.8	1063.7	52
54	0.2064	0.4202	1483	0.000674	4.720	1084.7	1062.7	54
56	0.2219	0.4518	1385	0.000722	5.054	1085.7	1061.6	56
58	0.2385	0.4856	1294	0.000773	5.410	1086.7	1060.6	58
60	0.2562	0.5217	1210	0.000827	5.785	1087.6	1059.6	60
62	0.2749	0.5598	1132	0.000883	6.043	1088.6	1058.5	62
64	0.2949	0.6005	1060	0.000943	6.604	1089.6	1057.5	64
66	0.3161	0.644	993	0.001007	7.048	1090.5	1056.4	66
68	0.3386	0.689	931	0.001074	7.52	1091.5	1055.4	68
70	0.3625	0.738	873	0.001145	8.02	1092.4	1054.3	70
72	0.3879	0.789	820	0.001220	8.54	1093.3	1053.3	72
74	0.4148	0.844	770	0.001300	9.10	1094.3	1052.2	74
76	0.4433	0.903	723	0.001383	9.68	1095.2	1051.2	76
78	0.4735	0.964	680	0.001471	10.30	1096.1	1050.1	78
80	0.5054	1.029	639	0.001564	10.95	1097.1	1049.0	80
82	0.539	1.098	601.4	0.001663	11.64	1098.0	1048.0	82
84	0.575	1.171	565.7	0.001768	12.37	1098.9	1046.9	84
86	0.613	1.248	532.2	0.001879	13.15	1099.8	1045.8	86
88	0.653	1.329	500.8	0.001997	13.98	1100.7	1044.7	88
90	0.695	1.415	471.4	0.002121	14.85	1101.6	1043.6	90
92	0.739	1.506	443.9	0.002253	15.77	1102.5	1042.5	92
94	0.787	1.602	418.2	0.002391	16.74	1103.4	1041.4	94
96	0.837	1.704	394.2	0.002537	17.76	1104.3	1040.3	96
98	0.890	1.812	371.8	0.002690	18.79	1105.2	1039.2	98
100	0.946	1.925	350.9	0.002850	19.95	1106.1	1038.1	100

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Temp. Fahr.	Pressure		Volume of One Pound (Cu. Ft.)	Weight of One Cubic Foot		Total Heat	Latent Heat	Temp. Fahr.
	Lb. per Sq. In.	Inches of Hg.		Pounds	Grains			
t	p	—	v''	γ	—	q''	r	t
102	1.004	2.044	331.4	0.003017	21.12	1107.0	1037.0	102
104	1.066	2.171	313.2	0.003193	22.35	1107.9	1035.9	104
106	1.131	2.303	296.2	0.003376	23.63	1108.7	1034.8	106
108	1.199	2.441	280.4	0.003566	24.96	1109.6	1033.7	108
110	1.271	2.588	265.6	0.003765	26.36	1110.5	1032.5	110
120	1.689	3.439	203.4	0.004916	34.42	1114.8	1026.9	120
130	2.219	4.518	157.5	0.00635	44.45	1119.0	1021.1	130
140	2.885	5.874	123.1	0.00812	56.86	1123.1	1015.2	140
150	3.714	7.56	97.2	0.01029	72.0	1127.1	1009.3	150
160	4.737	9.64	77.4	0.01293	90.5	1131.1	1003.2	160
170	5.988	12.19	62.09	0.01611	112.7	1135.0	997.1	170
180	7.506	15.28	50.23	0.01991	139.4	1138.8	990.9	180
190	9.335	90.01	40.94	0.02443	171.0	1142.5	984.6	190
200	11.523	23.46	33.60	0.02976	208.3	1146.2	978.2	200
210	14.122	28.75	27.77	0.03601	252.1	1149.7	971.7	210
212	14.697	29.92	26.75	0.03738	261.7	1150.4	970.4	212

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TABLE III

Properties of Saturated Vapor of Ammonia

Temperature, F.	Pressure Lb. per Sq. In.	Heat Content		Latent Heat			Entropy		Volume of One Pound	Temperature, F.
		of Liquid	of Vapor	of Vaporisation	Internal	External	of Liquid	Vaporisation		
t	p	i'	i''	r	ρ	ψ	s'	$\frac{r}{T}$	v''	t
−30	13.51	−67	536	603	554	49	−0.146	1.404	19.78	−30
−25	15.54	−62	537	599	549	50	−0.133	1.379	17.34	−25
−20	17.82	−57	538	595	545	50	−0.121	1.354	15.23	−20
−15	20.36	−51	540	591	540	51	−0.109	1.329	13.43	−15
−10	23.18	−46	541	587	536	51	−0.098	1.305	11.88	−10
−5	26.32	−41	542	583	532	51	−0.086	1.281	10.53	−5
0	29.78	−35	543	578	527	51	−0.074	1.257	9.36	0
5	33.52	−30	544	574	522	52	−0.062	1.234	8.38	5
10	37.80	−24	545	569	517	52	−0.051	1.212	7.46	10
15	42.41	−19	546	565	513	52	−0.039	1.190	6.69	15
20	47.46	−13	547	560	508	52	−0.027	1.168	6.01	20
25	52.98	−8	548	556	503	53	−0.016	1.147	5.41	25
30	59.00	−2	549	551	498	53	−0.005	1.125	4.88	30
35	65.52	3	550	547	493	53	0.007	1.104	4.41	35
40	72.6	9	551	542	489	53	0.018	1.084	4.01	40
45	80.3	15	552	537	483	54	0.029	1.064	3.63	45
50	88.6	20	552	532	478	54	0.041	1.044	3.30	50
55	97.5	26	553	527	473	54	0.052	1.024	3.01	55
60	107.1	32	554	522	468	54	0.063	1.004	2.74	60
65	117.5	37	554	517	463	54	0.074	0.985	2.51	65
70	128.3	43	555	512	458	54	0.085	0.966	2.30	70
75	140.5	49	555	506	452	54	0.096	0.947	2.11	75
80	152.8	55	556	501	447	54	0.107	0.928	1.94	80
85	166.8	61	557	496	442	54	0.118	0.910	1.78	85
90	181.2	67	557	490	436	54	0.128	0.892	1.64	90
95	196.7	73	557	484	430	54	0.139	0.873	1.51	95
100	213.0	79	558	479	425	54	0.150	0.855	1.40	100

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